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Corrosion Inhibition Potential of Two Isoxazole Derivatives: Experimental and Theoretical Analyses

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Abstract

The 5-phenylisoxazole (P) and 3-phenyl-5-isoxazolone (PI) were looked at as corrosion inhibitors for mild steel in a 2 M HCl solution using gravimetric and quantum analyses at 30ºC – 60ºC. The results obtained revealed that inhibition efficiency increased with an increase in inhibitor concentrations ranging from 2 x 10^{-4} M to 10 x 10^{-4} M. The maximum inhibition at the optimum concentrations of P and PI in HCl solution at 30ºC is 66 and 80 %, respectively. The negative values of Gibb's free energy (ΔG^{o}_{ads}) ranged from -17.62 kJ/mol to -21.45 kJ/mol for the inhibitors indicating spontaneous adsorption of the inhibitors on a mild steel surface, and the adsorption mechanism is physisorption. The positive values of ΔH° reflect the endothermic behavior of the adsorption of studied inhibitors on the mild steel surface. The negative values for entropy imply that the adsorption process is accompanied by a decrease in entropy. The inhibition efficiency increases with increasing E_{HOMO} indicating that these molecules have the propensity to offer electrons to the appropriate acceptor molecule with low energy empty molecular orbital; whereas the low value of E_{LUMO} suggests that, the molecule easily accepts electrons from donor molecules. The energy gaps (ΔE) of the studied inhibitors were 8.04 and 8.63 eV for PI and P respectively. Fukui index was proposed to foresee electrophilic and nucleophilic sites of the inhibitor molecule.

1. Introduction

The usefulness of Iron-based materials in many fields such as industries, engineering, submarine, etc aroused from its low cost, high mechanical strength, and malleability [1–3]. Unfortunately, the vulnerability of iron-based materials to corrosive attack by the action of destructive environments cannot be ignored [4]. However, it is a known fact that environmental pollutants have a thoughtful effect on the durability of metals [1]. The report in 2001 stressed that the United State of America spent over $276 billion per year [5]. Out of these expenses, they detected that about $121 billion was spent on corrosion control [5]. Most short down in petroleum and gas industries are triggered by corrosion [6]. For instance, in Austin, Texas, on January 9, 2012, gas leakage from a corroded pipe feared a man to death. Also, about 117,000 gallons of gasoline in Wellington spilled from the Sunoco pipeline on January 12, 2012. Sometimes companies are forced to evacuate because of a major leak in their Pipeline [7]. On January 31, 2012, a fuel pipeline leaked along Milwaukee, Wisconsin Mitchell International

Airport. It is a dilemma that creates a menace by influencing the safety of structures, which can result in severe injuries.

The oxidation-reduction reaction is the rudimentary method of metallic corrosion in aqueous solutions which comprises of an anodic reaction (metal dissolution) and a cathodic reduction of any oxidant present in the electrolyte solution (e.g. H^+ or O^{2-}) [8]. Corrosion inhibition based on adding special chemicals into the solution in contact with the metal of interest is among the most suitable protective methods for metallic corrosion [9].

Pyrazole derivatives are one of the important classes of heterocyclic compounds which has various applications in several fields. It has been established by many researchers that over the past decades, pyrazolic compounds have the efficacy of corrosion inhibition in certain aggressive environments for mild steel [10–12]as well as for many other metals and alloys [13–16]. In addition, pyrazole derivatives possess biological activity such as anticancer, anti-microbial, anti-viral, anti-tubercular, anti-inflammatory, anti-fungal, anti-convulsant and they are also used as dyes, fungicides, herbicides, insecticides, and pesticides [17–21]. It is a well-known fact that some organic compounds are toxic and produce healthy and environmental problems as such paved the way for the development of novel eco-friendly corrosion inhibitors (EFCI). Elmsellem *et al.* [22] reported an IE of 95% for a derivative containing carbohydrazide and pyrazole in 1 M HCl. Yadav *et al.* [23]showed for a pyrazolic derivative in 15% HCl solution an IE of 95.9% at 250 ppm. Paul *et al.* [24] reported two carbohydrazide-pyrazole derivatives to have impressive IEs of 98.26% and 96.21% at 300 ppm in 15% HCl solution. Hameed [25] presented a pyrazole derivative in 1 M HCl with an IE of 95%. Farhadiana *et al.* [26] synthesized a new EFCI by using Castor oil and overcome the low biodegradability and poor performance of corrosion inhibitions at high temperatures. The pyrazolic compounds are eco-friendly inhibitors because they possess a potent chemical activity allied with high solubility in acidic environments, compared to other organic compound families [27–29]. Verma [27]reported a pyrazolic derivative produced by microwave irradiation method and conforming with the concepts of green chemistry showed an inhibition efficiency of 94.88% (IE) at 300 ppm in 1 M HCl. Boudjellal *et al.* [30] reported a pyrazolic carbothioamide derivative that showed an IE of 96.60% at 5×10^{-4} M in 1 M HCl. Mechbal *et al.* [31] reported the corrosion prohibition capacity of two synthesized eco-friendly pyrazole derivatives namely, N1,N1, N5,N5-tetrakis(3,5-dimethyl-1H-pyrazole-1-yl)methyl)naphthalene-1,5-diamine (NPDM) and N1,N1,N5,N5-tetrakis(1H-pyrazole-1-yl) methyl)naphthalene-1,5-diamine (NPD) have impressive IEs of 89.02 % and 92.10 % at 10^{-3} mol/L in 0.5 M H_2SO_4. Rahmani *et al.* [32] reported the corrosion inhibition performances of (4-ethyl-2-phenyl-4,5-dihydro-1,3-oxazol-4-yl)-methanol (C1); 4-{[(4-ethyl-2-phenyl-4,5-dihydro-1,3-oxazol-4-yl)methoxy]methyl}- benzene-1-sulfonate (C2) and 4-[(azidoxy)methyl]-4-ethyl-2-phenyl-4,5-dihydro-1,3- oxazole (C3) mild steel in molar hydrochloric solution using gravimetric, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques as well as quantum chemical calculations. Results obtained reveal that these compounds reduce significantly the corrosion rate of mild steel, their inhibition efficiencies increased with inhibitor concentration. This behavior means that the inhibitive effect of the studied oxazole derivatives occurs through the adsorption of inhibitor molecules on the metal surface. Benzai *et al.* [33] reported the study of the inhibition of mild steel corrosion in a molar hydrochloric acid medium by some benzoxazol derivatives compounds. The results obtained through gravimetric and both transient and stationary electrochemical methods showed a satisfied coherence. Theoretical calculations also revealed a good correlation with the experimental results for the compounds.

Based on this, in the current paper, we are to explore the corrosion inhibition capacity of two eco-friendly isoxazole derivatives namely, 5-phenylisoxazole (P) and 3-phenyl-5-isoxazolone (PI) in 2 M

HCl by using gravimetric and computational methods. The selection of these inhibitors for this study was from the accomplishment of the crucial requirements of corrosion inhibitors as reported by Umoren (2008). Also, they had not been used as mild steel corrosion inhibitors in acidic medium to the best of our knowledge. From this point of view, the study shall involve investigating corrosion inhibition properties of the isoxazole derivatives for mild steel in an acidic medium. Moreso, it is expected that with the multiple adsorption sites, they shall be able to form complexes with the metal ions and on the metal surface [34]. The organic compounds are adsorbed on the metallic substrate and thereby developed a thin protective layer, which protects the metal from the corrosive attack of the surroundings by bringing down the corrosion rate [35]. A comparative study was performed to inspect the inhibition activity of these derivatives in connection with their molecular geometries (extent of planarity), global and local electronic properties in a destructive acid aqueous medium. Moreover, their deformation capacity to adhere to the mild steel surface was investigated through the calculations supported by the DFT method of the two isoxazole derivatives, namely: P and PI (Figure 1).

This study shall aid the understanding of corrosion mechanisms and minimize corrosion problems. The molecular structures of the studied compounds are shown in Figure 1 and the compounds were purchased from Sigma Aldrich.

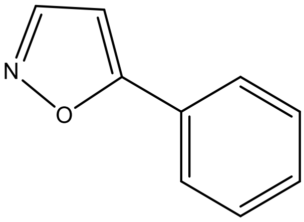

Figure 1a. Structure of 5-phenylisoxazole (P)

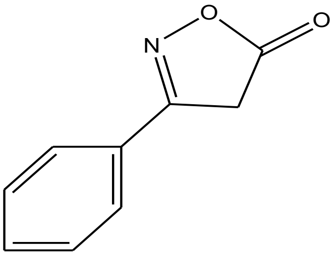

Figure 1b. Structure of 3-phenyl-5-isoxazolone (PI)

2. Methodology

2.1 Gravimetric experiments

The gravimetric experiments were conducted on mild steel coupons of dimensions 5.0 x 4.0 cm after being polished with SiC abrasive papers, 320, 400 and 600 grit, respectively and degreased in absolute ethanol, dried in acetone and store up in moisture-free desiccators before use [34]. Different concentrations (2.0 x 10^{-4} M – 10 x 10^{-4} M) of the studied inhibitors were prepared by dilution of the corresponding concentrated solutions using distilled water and the solutions in the absence of these inhibitors were taken to be blank. The pre-cleaned and weighed coupons were immersed in beakers containing 100 ml test solutions maintained at 303 – 333 K**.**

Weight loss was determined by removing the coupons from test solutions at 2 h intervals progressively for 10 h, washing in distilled water, scrubbing with a bristle brush, drying in acetone, and re-weighed [36]. The weight loss was taken to be the difference between the initial weight and the weight of the coupons at a given time interval.

2.2 Molecular modeling

Corrosion inhibition mechanisms were studied using quantum chemical calculations. Thus, the possible physical properties were determined to know which could contribute to inhibition. Full optimization was done using molecular mechanics, *Ab initio,* and DFT level [37]. PM7 Hamiltonian in the MOPAC 2014 software was used in computing semi-empirical parameters for the molecules [38]. Single point DFT calculations were also carried out using Hyperchem release 8.2 packages**.** DFT setting (MP2 inclusive) in the package were, Basic set: 321-G, iteration = 50, spin pairing =

unrestricted Hartree Fock, convergence limit = 1E-0.05 and Spin multiplicity = 1 (for zero charge and 2 for +1 and -1 charges). The relation between the inhibition efficiency of these inhibitors and the quantum chemical parameters was considered [39].

3. Results and Discussion

3.1 Weight loss studies

To ascertain the tendency of the studied inhibitors to minimize the corrosion of mild steel in the acidic medium, the gravimetric experiment was carried out [38]. From the results in table 1, weight loss measurement increases with an increase in time but decreased with an increase in concentrations of the studied inhibitors. A similar trend was observed by many researchers [12,40–44]. Figure 2 demonstrated the weight loss measurements with time at 30°C and related trends were observed at 40, 50, and 60°C. The plot in figure 2 shows an increase in corrosion rates with contact time for all systems and a decrease in corrosion rates due to the addition of the studied inhibitors which indicates that the studied compounds retard the mild steel corrosion in the corrosive environment [40]. A similar result was reported by Paul *et al*. [24].

Table 1. Calculated values of corrosion rate (CR), surface coverage (θ), and inhibition efficiency (I) of mild steel corrosion in different concentrations of P and PI

		303 K			**313 K**			**323 K**			**333 K**		
Inhibitor	Conc. (M) x 10^{-4}	CR (mm/yr) x 10^{-3}	θ	I (%)	CR (mm/yr) x 10^{-3}	θ	I (%)	CR (mm/yr) x 10^{-3}	θ	I (%)	CR (mm/yr) x 10^{-3}	θ	I (%)
P	Blank	3.00	-	-	4.96	-	-	6.34	-	-	8.41	-	-
	2	2.04	0.32	32	3.52	0.29	29	4.69	0.26	26	6.64	0.21	21
	4	1.56	0.48	48	2.78	0.44	44	3.80	0.40	40	5.80	0.31	31
	6	1.47	0.51	51	2.53	0.49	49	3.61	0.43	43	5.47	0.35	35
	8	1.26	0.58	58	2.33	0.53	53	3.42	0.46	46	5.05	0.40	40
	10	1.02	0.66	66	1.79	0.64	64	2.47	0.61	61	4.46	0.47	47
PI	Blank	3.00	-	-	4.96	-	-	6.34	-	-	8.41	-	-
	2	2.74	0.42	42	2.98	0.40	40	4.06	0.36	36	7.14	0.27	27
	4	2.47	0.51	51	2.83	0.43	43	3.99	0.37	37	5.97	0.29	29
	6	1.97	0.62	62	2.43	0.51	51	3.68	0.42	42	5.13	0.39	39
	8	1.45	0.70	70	1.89	0.62	62	2.92	0.54	54	4.88	0.42	42
	10	1.30	0.80	80	1.30	0.74	74	2.03	0.68	68	4.37	0.48	48

The studied compounds could be seen to exhibit corrosion-inhibiting effects at all concentrations reaching a maximum inhibition efficiency of 66 % and 80 % for P and PI respectively, at the optimum concentration of 10 x 10^{-4} M (Table 1). The values of the weight loss and percentage inhibition efficiency (%) obtained from the weight loss method at different concentrations of the studied inhibitors were found to be more effective at 303 K (Table 1) [41]. This result corresponds to that of Paul *et al.*[24] and Dohare *et al.*[45] which is attributed to partial desorption of the molecules from the Mild Steel surface.

3.2 Effect of temperature

To understudy the temperature dependence of corrosion rates in uninhibited and inhibited solutions, the gravimetric measurements were carried out in the temperature range 303 K – 333 K in the presence of different concentrations of 5-Phenylisoxazole and 3-Phenyl-5-isoxazolone in 2 M HCl solutions [45]. The inhibition efficiencies as a function of concentrations are presented in table 2. The results show that inhibition efficiency increased with the inhibitors' concentration but decreased with prolonged exposure [46]. Similar behavior was reported by many researchers [24,27,45,47,48].

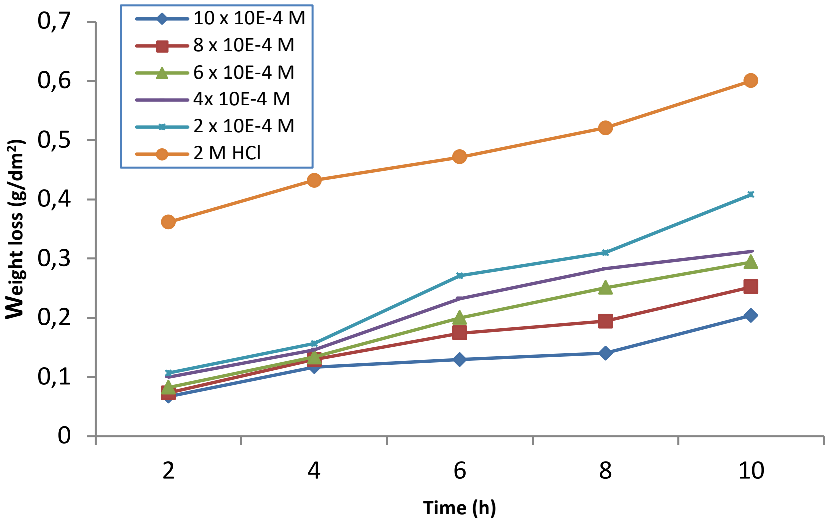

Figure 2. The plot of weight loss versus time for mild steel in 2 M HCl solution containing different concentrations of 5-phenylisoxazole at 303 K.

High efficiencies of 66 % for P and 80 % for PI were noticed with the studied concentrations after 10 h, which points out, that the surface coverage of the substrate by these inhibitors attended an optimum level within 10 h. From the results, the highest concentration of these inhibitors at 303 K gives maximum inhibition efficiency. The results show that inhibition efficiency decreases as the temperature increases indicating the physisorption process as reported by Khaled et al. [49]. From the results, it could be observed that inhibitor concentration increases as the corrosion rate decreases, thus leading to an increase in the inhibition efficiency.

The adsorptions of these inhibitors on mild steel surfaces were studied using adsorption isotherms [50]. Adsorption isotherms gave vital information on the interaction of inhibitor and metal surfaces as observed by Umoren [51]. The degree of surface coverage values (θ) at different inhibitors concentrations in 2 M HCl solutions were assessed from weight loss measurements at 303 K – 333 K and tested graphically for fitting to a suitable adsorption isotherm [52]. The adsorption isotherm model considered was Temkin isotherm as represented by equation (1) [53]:

$$\exp(f\theta) = K_{ads}C \qquad (1)$$

Where K_{ads} is equilibrium, constant of the adsorption process, C is inhibitor concentration and f is a factor of energetic inhomogeneity. The equilibrium, K_{ads} was determined from the slopes of θ versus ln C graphs as shown in figures 3 and 4 for P and PI, respectively.

Among the adsorption isotherm models considered, the best-fitted straight line was obtained from the Temkin isotherm as the correlation coefficients (R^2) were in the range $0.9784 \geq R^2 \geq 0.9157$. From the results in table 2, it is seen that the values of molecular interaction parameter 'a' are negative in all cases showing attraction in the adsorption layer. A similar result was observed by Obot and Obi-Egbedi [53]. The equilibrium constant of the adsorption process, K_{ads} denotes the strength between adsorbate and adsorbent. The higher the values of K_{ads}, the more efficient the adsorption and hence, better inhibition efficiency [54]. It is obvious from table 2 that values of K_{ads} are very low indicating weak interaction between the inhibitor and the mild steel surface. This implies that electrostatic interaction (Physisorption) has taken place between the inhibitor molecules and the metal surface [55]. The negative values of ΔG°_{ads} observed in Table 2 reveal that the adsorption of the inhibitors on mild steel surface in 2 M HCl solution is a spontaneous process [55].

The activation energy values in Table 3 indicate that the presence of studied inhibitors (P and PI) increases the activation energy of the metal dissolution reaction. The adsorption of the studied inhibitors is believed to take place on the higher energy sites and the presence of the inhibitor, which results in the blocking of the active sites, must be related to an increase in the activation energy of mild steel corrosion in the inhibited state [56]. The higher value of Ea in the presence of inhibitors compared to that in its absence and the decrease in the inhibition efficiency (%) with rising in temperature is deduced as an indication of physisorption.

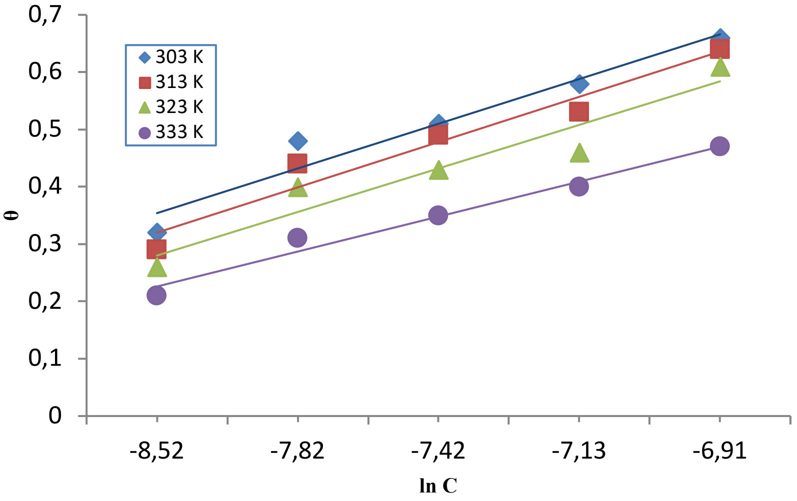

Figure 3. Temkin adsorption isotherm plot of θ versus ln C for Mild steel in 2 M HCl solution containing different concentrations of 5-Phenylisoxazole

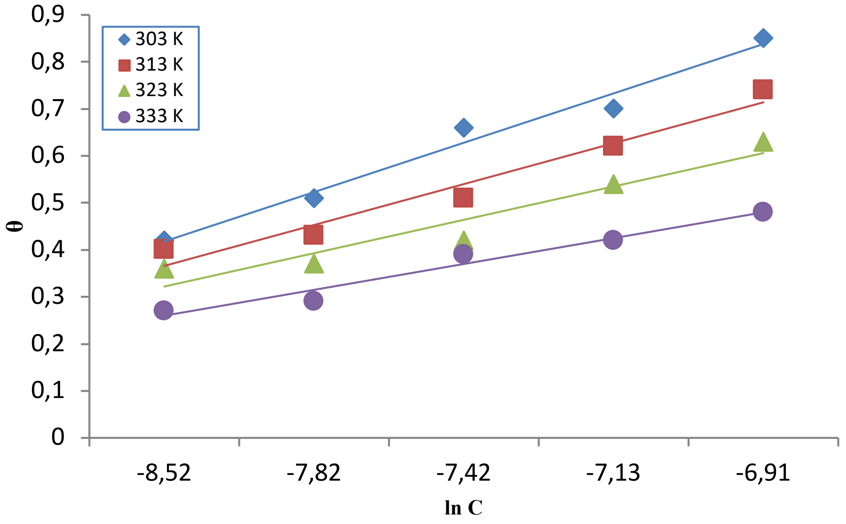

Figure 4. Temkin adsorption isotherm plot of θ versus ln C for Mild steel in 2 M HCl solution containing different concentrations of 3-Phenyl-5-isoxazolone

In acidic solution, the corrosion rate is related to temperature by Arrhenius equation as shown in equation (2).

$$RT\ln CR = RT\ln A - Ea \qquad (2)$$

where CR is the corrosion rate determined from the weight loss measurement, E_a, the apparent activation energy, A the Arrhenius constant, R the molar gas constant and T is the absolute temperature.

The apparent activation energy was determined from the slopes of log CR versus I/T graphs depicted in figures 5 and 6 for P and PI, respectively.

Table 2. Adsorption parameters from Temkin isotherm for mild steel in 2 M HCl solution with different concentrations of P and PI at 303 – 333 K.

	Temp (K)	**Adsorption Parameters**				
		K_{ads} (mol/l)	f	a	-ΔG (kJ/mol)	R^2
P	303	34.47	12.82	-6.41	19.03	0.9447
	313	21.12	12.66	-6.33	18.39	0.9473
	323	14.59	13.16	-6.58	17.98	0.9157
	333	15.03	16.39	-8.20	18.62	0.9772
PI	303	19.69	9.52	-4.76	17.62	0.9784
	313	24.78	11.49	-5.75	18.80	0.9581
	323	34.47	14.09	-7.05	20.29	0.9179
	333	41.68	18.18	-9.09	21.45	0.9634

Enthalpy of activation, ΔH° and entropy of activation, ΔS° were gotten from transition state equation as shown in equation (3):

$$CR = \frac{R^*T}{Nh}\exp\left(\frac{\Delta S^\circ_{ads}}{R^*}\right)\exp\left(\frac{-\Delta H^\circ_{ads}}{R^*T}\right) \tag{3}$$

Where N is Avogadro's number, h is Planck's constant, ΔS^O_{ads} is standard entropy change, ΔH^O_{ads} is standard enthalpy change, R is universal gas constant and T is temperature. The computed values of the activation parameters of activation for the dissolution of mild steel at different temperatures are presented in table 3. Examination of these data in table 3 revealed that the positive values of ΔH_o reflect the endothermic behavior of the adsorption of the studied inhibitors (P, PI) on the mild steel surface [51]. The ΔS_o values are negative indicating that the adsorption is an endothermic process [51]. The adsorption between the organic compound in the aqueous phase [org (sol)] and water molecules at the electrode surface [H_2O(ads)] is regarded as a quasi-substitution process [55]. Thus, the adsorption of P and PI is accompanied by the desorption of water molecules from the electrode surface.

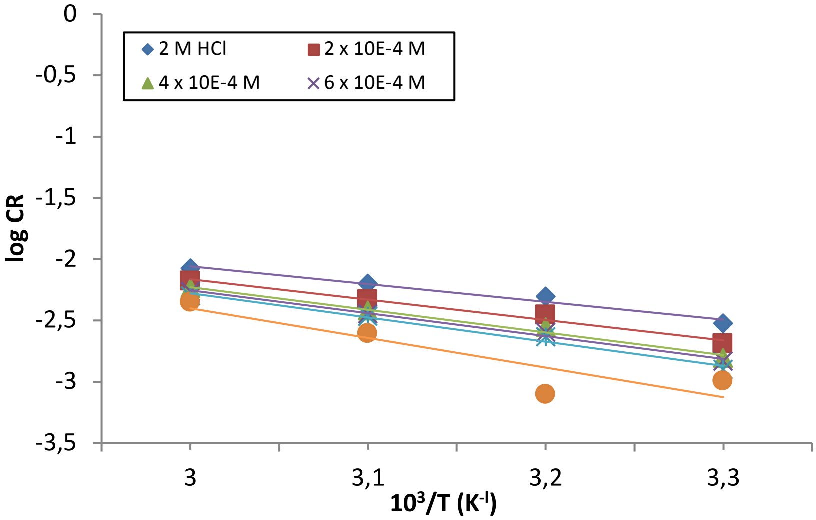

Figure 5. Arrhenius plot of log CR versus 1/T for mild steel in 2 M HCl solution containing different concentrations of 5-phenylisoxazole

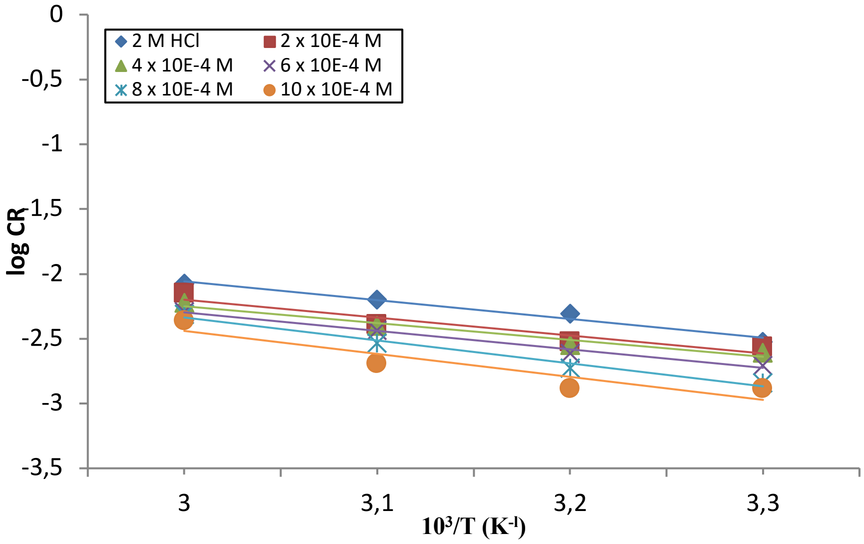

Figure 6. Arrhenius plot of log CR versus 1/T for mild steel in 2 M HCl solution containing different concentrations of 3-phenyl-5-isoxazolone

Consequently, the adsorption process is endothermic and associated with a decrease in entropy of the solute; the same is factual for the solvent. The thermodynamic parameters obtained are the algebraic sum of the adsorption of these organic molecules and the desorption of water molecules [56]. Thus, the increase in entropy is due to the increase in solvent entropy [57]. The negative values for entropy imply that the adsorption process is attended by a decrease in entropy, which is the driving force for the adsorption of these inhibitors (P and PI) on the mild steel surface [58].

Table 3. Activation parameters for mild steel coupons in 2 M HCl solution with different concentrations of P and PI at 303 – 333 K.

Inhibitor	Conc. (M) x 10^{-4}	Activation Parameters		
		E_a (kJ/mol)	ΔS° (J/mol.K)	ΔH° (kJ/mol)
P	Blank	27.751	-150.530	25.136
	2	31.817	-140.365	29.198
	4	35.357	-130.978	32.739
	6	36.050	-129.305	33.434
	8	37.806	-124.565	35.193
	10	39.485	-121.208	36.868
PI	Blank	27.751	-150.530	25.136
	2	38.515	-120.136	35.902
	4	36.973	-125.734	34.358
	6	38.272	-122.810	35.659
	8	42.115	-112.229	39.499
	10	49.397	-91.8760	46.784

3.3 Global molecular reactivity

The quantum chemical parameters computed with PM7 Hamiltonian in the MOPAC 2014 software using the gas phase for the studied compounds are presented in table 4. Similar software has been used by Eddy et. al. [36,59]. The difference in energy of the highest occupied molecular orbital (E_{HOMO}) and that of the lowest unoccupied molecular orbital (E_{LUMO}) are important parameters for defining the reactivity of a chemical species. From the results obtained, it is observed that the values of E_{HOMO} are all less than those of E_{LUMO}, indicating strong adsorption arising from effective electronation of the iron empty orbital by the inhibitor molecule [59, 60].

Table 4. PM7 semi-empirical parameters for the studied isoxazole derivatives

Semiempirical Parameters	P	PI
Hf (kCal/mol)	45.20	3.13
TE (eV)	-1679.25	-1974.57
EE (eV)	-8247.38	-9745.87
CCR (eV)	6568.14	7771.30
Dipole (eV)	3.19	6.62
IE (eV)	9.51	9.18
EHOMO (eV)	-9.51	-9.18
ELUMO (eV)	-0.88	-1.14
EL-H (eV)	8.63	8.04
f^{+}_{k}	-0.0072	5.1133
f^{-}_{k}	0.5729	4.7468
Cosmo area (Å2)	175.95	184.59
Cosmo volume (Å3)	173.70	182.52
Hydration energy (kCal/mol)	-7.64	-8.35
Logarithm of P	0.56	0.27
Refractivity	48.21	48.90
Polarizability	16.54	17.03
Maximum IE %	66	80

Hf = Heat of formation, TE = Total energy, EE = Electronic energy, CCR = Core-core repulsion energy, IE = Ionization energy, log p = hydrophobicity

The formation of a feedback bond is usually characterized by increasing and decreasing values of E_{HOMO} and E_{LUMO} respectively, which is proposed for the observed trend [60-62]. A smaller energy gap implies high reactivity to a chemical species [59]. From Table 4, it is obvious that the energy gap, ΔE of the studied inhibitors, PI and P are 8.04 and 8.63 eV respectively. As a result, the inhibition efficiency of the inhibitor molecules is 80 for PI and 66 for P. Figures 7 and 8 showed the distribution of HOMO and LUMO of these isoxazole derivative molecules. From figures 7 and 8, it could be seen that the distribution of HOMO and LUMO is mainly located at the benzene ring, nitrogen, and oxygen atoms in substituent groups. This kind of distribution favors the parallel adsorption of isoxazole inhibitors onto the metal surface via two modes [62]. One mode is that the inhibitor molecules donate electrons to the unoccupied d orbital of the Fe atom forming a coordinate bond and the other mode is that the inhibitor molecules accept electrons from the Fe atom to form a back-donating bond [63].
Besides, the expected trend for the variation of inhibition efficiency is consistent with the experimental results. Semiempirical calculations estimate ionization energy through the value of E_{HOMO}. Ionization energy measures the ability of a molecule to lose electrons. In this case, two systems, Fe (in mild steel) and inhibitor are brought together, hence, electrons will flow from the lower system with lower electronegativity (inhibitor) to the system with higher electronegativity until the chemical potential becomes equal [59]. Based on the IE, the trend for the variation of inhibition potentials of the studied Isoxazole derivatives agrees with experimental findings.

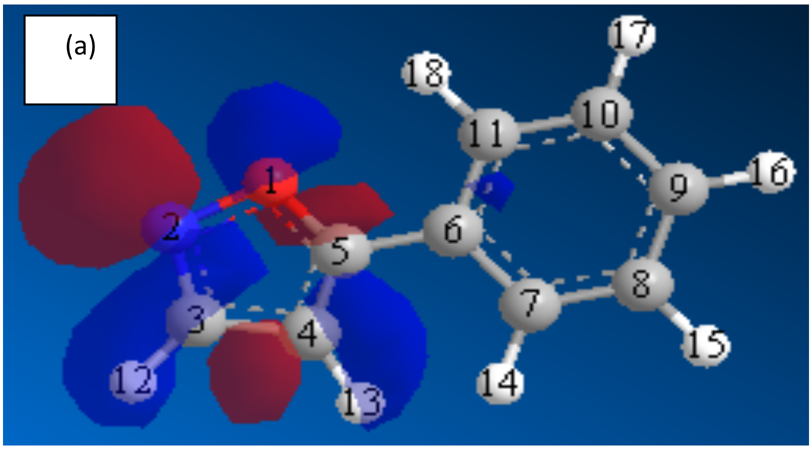

Figure 7a. HOMO orbitals of the 5-phenylisoxazole molecule (P)

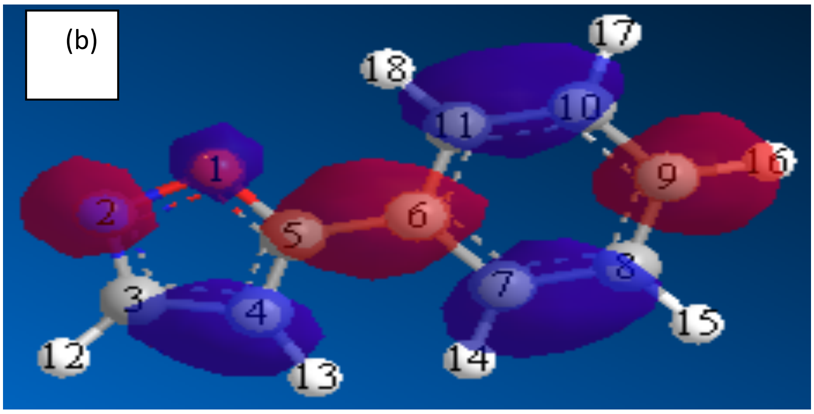

Figure 7b. LUMO orbitals of the 5-phenylisoxazole molecule (P)

Log P is a substituent constant accounting for the hydrophobicity of the actual molecule. Hydrophobicity of organic molecules increases with decreasing water solubility. In corrosion studies, hydrophobicity is related to the mechanism of formation of the oxide/ hydroxide layer on the metal surface (which reduces the corrosion process drastically) [59].

The dipole moment of a compound (μ) refers to the tendency of a system to act as a dipole. The dipole moment is the measured polarity of a polar covalent bond [64]. It is defined as the product of the magnitude of the charge on the atoms and the distance between the two bonded atoms. From table 4, the negative total energy indicates that the studied inhibitor is a very stable molecule and is less prone to be broken apart. The dipole moment of the studied inhibitors, P and PI were 3.19 and 6.62 Debye respectively, which were higher than that of H_2O (1.87 Debye) [64]. The high values of dipole moment probably increase the adsorption between the compound and metal surface. Moreover, effective adsorption of the studied molecules on the mild steel surface is enhanced by higher area and volume. Literature discloses that there are several abnormalities in the correlation involving dipole moment and inhibition efficiency, noting that core-core repulsion (C–C) energy is a quantum chemical parameter that has a tremendous correlation with inhibition efficiency [64]. From table 4, inhibition efficiencies of the studied inhibitors increase with increasing value of C–C energy. Also, the inhibition efficiencies were found to increase with increasing values of Cosmo Area and Cosmo Volume [62]. The HOMO and LUMO molecular orbitals of the studied molecules are shown in figures 7 and 8. The blue and maroon orbital represent positive and negative sites of adsorption respectively.

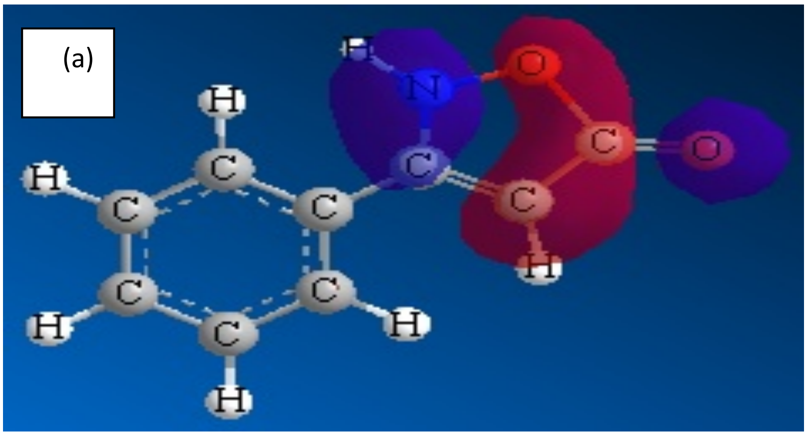

Figure 8a. HOMO orbitals of the 3-phenyl-5-isoxazolone molecule (PI)

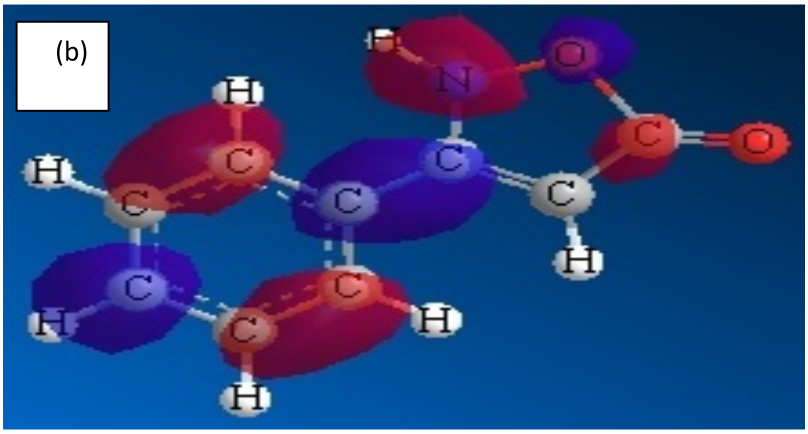

Figure 8b. LUMO orbitals of the 3-phenyl-5-isoxazolone molecule (PI)

3.4 Local molecular selectivity

The local molecular selectivity of the inhibitors was analyzed by condensed Fukui and condensed softness functions. The indices that allowed the distinction of each part of a molecule based on its chemical behavior due to different substituent functional groups were condensed Fukui and the condensed softness functions [45,59]. Local molecular reactivity was used to evaluate the active sites of the inhibitor molecules. Tables 5 and 6 showed the local reactivity parameters of these inhibitors.

The Fukui function is roused from the fact that an electron is transferred to an N electron molecule, and tends to distribute to minimize the energy of the resulting N + d electron system [59,65]. The resulting change in electron density is nucleophilic and electrophilic.

Tables 5 and 6 present calculated values of f^{+} and f^{-} for carbon, nitrogen, and oxygen atoms in PI and P molecules. The site for the nucleophilic attack is at the place where the value of f^{+} is maximum whereas the site for the electrophilic attack is controlled by the value of f^{-}. An atom with high f^{+} and f^{-} would have strong interaction with the metal surface by exchanging electrons [59, 66]. From the f^{+} and f^{-} presented in Tables 6 and 7, the active sites could be found. As for electrophilic attack index f^{+}, the active sites of inhibitor PI are mainly located on C(7), C(9), C(11) and O(1), and the active sites of inhibitor P are mainly located on C(8), C(4), C(11) and O(1). As for nucleophilic attack f^{-} of the inhibitors, the active sites are located mostly on the heteroatoms in the substituent groups [45,59,66]. The Fukui function is an effective parameter to describe the local reactivity [63]. From the results in Tables 5 and 6, it could be seen that some atoms possessed both high f^{+} and high f^{-}, and it meant that these atoms had strong a capability to attract and donate electrons [45]. Therefore, it was difficult to estimate their contribution to exchanging electrons with the metal surface.

Table 5: Fukui functions for carbon and electronegative elements in 5-phenylisoxazole

Atom No.	q_{Huckel}	q_N	q_{N-1}	q_{N+1}	f_k^-	f_k^+	$f^{(2)}$(r)
O (1)	0.117825	0.0319	-0.2443	-0.0131	0.2762	-0.0450	-0.3212
N (2)	-0.203044	0.0384	1.6524	-0.0412	-1.6139	-0.0796	1.5343
C (3)	0.0579987	0.0096	-0.4773	-0.0295	0.4870	-0.0391	-0.5261
C (4)	-0.223633	0.0388	-0.0335	0.0303	0.0723	-0.0085	-0.0808
C (5)	0.273412	-0.0012	-0.2087	-0.0561	0.2076	-0.0549	-0.2625
C (6)	0.0517633	-0.0393	-0.3475	-0.0518	0.3082	-0.0125	-0.3207
C (7)	-0.0622497	0.0439	0.1843	0.0147	-0.1404	-0.0292	0.1112
C (8)	-0.0229482	0.0468	0.1544	0.0396	-0.1076	-0.0072	0.1004
C (9)	-0.0501528	0.0513	-0.5216	0.0277	0.5729	-0.0236	-0.5965
C (10)	-0.0227729	0.0415	0.2922	0.0219	-0.2507	-0.0196	0.2311
C (11)	-0.051172	0.0593	0.1059	0.0477	-0.0466	-0.0116	0.035

Table 6: Fukui functions for carbon and electronegative elements in 3-phenyl-5-isoxazolone

Atom No.	q_{Huckel}	q_N	q_{N-1}	q_{N+1}	f_k^-	f_k^+	f(2)(r)
O(1)	-0.0756275	-1.9876	-2.2236	-2.0510	0.2360	-0.0634	-0.2994
N(2)	0.65018	-3.0051	-3.2890	-4.4604	0.2839	-1.4553	-1.7392
C(3)	0.0987542	-4.6195	-4.9151	-6.3638	0.2956	-1.7444	-2.04
C(4)	-0.361714	-3.3598	-6.0798	-4.7922	2.7201	-1.4324	-4.1525
C(5)	0.398978	-6.0502	-10.7970	-8.7639	4.7468	-2.7138	-7.4606
C(6)	-0.781499	-1.7679	-1.7997	-1.8203	0.0318	-0.0524	-0.0842
C(7)	0.0595671	-1.4809	4.3599	3.6324	-5.8408	5.1133	10.9541
C(8)	-0.0579317	4.1036	3.9956	4.0243	0.1080	-0.0793	-0.1873
C(9)	-0.0227236	3.9199	4.0028	4.0047	-0.0829	0.0848	0.1677
C(10)	-0.0489966	4.0070	4.0059	4.0054	0.0012	-0.0016	-0.0028
C(11)	-0.0237383	3.9493	4.0029	4.0045	-0.0536	0.0552	0.1088
C(12)	-0.0526915	4.0883	4.0105	3.9807	0.0778	-0.1077	-0.1855

Herein, another parameter known as a dual descriptor was introduced to resolve this situation. This index was expressed as 'be at the same time an indicator for both the nucleophilic and electrophilic regions of a molecule'. The values of f^2(r) for the studied molecules are presented in Tables 6 and 7. As for P: N(2), C(7), C(8), and C(10) are the electrophilic sites with f^2(r) of 1.5343, 0.1112, 0.1004, and 0.2311 respectively. These four atoms accepted electrons from the metal surface, whereas C(3) and C(9) are the nucleophilic sites with f^2(r) of -0.5261, and -0.5965 respectively. As for PI: C(7), C(9), and C(11) are the electrophilic sites with f^2(r) of 10.9541, 0.1677, and 0.1088 respectively. These three atoms accepted electrons from the metal surface, whereas N(2), C(4), and C(5) are the nucleophilic sites with f^2 (r) of -1.792, -4.1525, and -7.4606 respectively.

Conclusion

The studied compounds were realized to be effective inhibitors for mild steel corrosion in a 2 M HCl solution. The adsorption of these inhibitors on a mild steel surface in 2 M HCl solution follows Temkin adsorption isotherm and is a spontaneous exothermic process accompanied by an increase in entropy. The phenomenon of physical adsorption was proposed from the values of kinetic/thermodynamics parameters obtained. Quantum chemical parameters and local selectivity indices predicted the direction of the inhibition reactions and the sites for nucleophilic/electrophilic attacks concerning the studied inhibitors.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors declare no conflicts of interest.

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