Theoretical study of the inhibition and the adsorption properties of N-containing aromatic compounds as corrosion inhibitors of mild steel in hydrochloric acid

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Abstract

Quantum chemical approach was used to investigate the electronic structures and properties of four N-containing aromatic compounds namely quinoline (Q), 8-hydroxy quinoline (HQ), 2-carboxy aniline (CA) and 2- methoxy aniline (MA), to ascertain the correlation between their molecular structure, the experimental inhibition efficiency (IE%) and some of the computed parameters. DFT calculations were performed to evaluate the quantum chemical parameters such as the highest occupied molecular orbital energy (EHOMO), the lowest unoccupied molecular orbital energy (ELUMO), energy gap (ΔE), dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (r), ionization potential (I) and the fraction of electrons transferred from the inhibitor molecule to the metal surface (ΔN). In addition, the adsorption behaviour of these compounds on Fe (110) surface and their adsorption energy was investigated. The theoretically obtained results were found to be in good agreement with the experimental data recently reported. The relations between the inhibition efficiency and some quantum parameters are discussed and correlations are proposed.

Keywords: Acidic Corrosion, Inhibitor, DFT calculations, HOMO and LUMO, Quantum parameters, Adsorption locator.

1. Introduction

The corrosion phenomenon that is naturally occurring phenomenon is one of the main problems facing industrial processes and has remarkable negative economic effects [1]. Acidic solutions, which are widely used in acid pickling, acid cleaning and acid de-scaling and acidification of oil wells, accelerate the corrosion rate. Mild steels are the most widely used materials in variety of industries as well as daily life applications [2]. Therefore, steels are frequently exposed to the action of bases or acids in the industries. Corrosion inhibitors is one of the most effective method for corrosion control and metallic surfaces protection [3]. The study of corrosion inhibition of mild steel using organic inhibitors mainly in acidic media is one of the most important subjects of current research. A survey of the literature on corrosion inhibitors reveals that most organic inhibitors employed as corrosion inhibitors contain heteroatoms with electronic lone pair (N, O, S and P), π systems, conjugated bonds, or/and aromatic rings in their molecular structure. These organic inhibitors are adsorbed on the metal structures via a coordinate covalent bond or the physical interactions [4, 5]. The produced a uniform film isolates the metal surface from the aggressive solutions and as result, reduces the corrosion level. In general, the adsorption depends on (i) the chemical structure of inhibitor, (ii) the nature and the state of the metal surface and (iii) the type of corrosive environment [6]. The research and development of new and more effective organic corrosion inhibitors requires the understanding of the electronic proper-

ties of the inhibitors and the elucidation of the interaction between the metal surface and inhibitor molecules.

Recently, most of the corrosion publications cover a quantum chemical calculation which is a very powerful tool for studying the corrosion inhibition mechanism [7]. The theoretical calculations are used to investigate the relationship between the corrosion inhibition efficiencies and their inhibitor molecular structures [8-10]. In the light of that, inhibition efficiency is correlated to the molecular and structural parameters that can be obtained through theoretical calculations such as chemical selectivity, reactivity, and charge distribution [7, 11, 12]. The quantum chemical results are the frontier molecular orbital; HOMO (higher occupied molecular orbital) energy, the LUMO (lower unoccupied molecular orbital) energy, chemical potential (μ) and hardness (η), electronegativity (χ), and electron transfer number (ΔN) and others [10, 13, 14]. In addition, understanding adsorption process is of key rule in corrosion studies. Monte Carlo calculation help in finding stable adsorption active sites on surface of mild steel through finding the low-energy adsorption sites on substrates [15].

Experimental corrosion rates and corrosion inhibition efficiencies of mild steel in 1M HCl solutions using organic inhibitors namely quinoline (Q), 8-hydroxy quinoline (HQ), 2-carboxy aniline (CA) and 2-methoxy aniline (MA) were already experimentally determined and details of this research were given previously [16]. In this paper, the results of corrosion rates and corrosion inhibition efficiencies were used for additional comparison between experimental and theoretical studies. The inhibitor molecules (Figure 1.1) were divided into the following two classes: (1) title quinoline molecules, which included the Q and HQ molecules, and (2) aniline derivatives, which included AM and AB molecules.
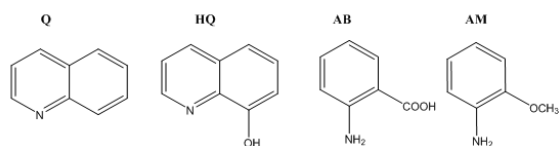
Figure 1.1: The molecular structures of the investigated inhibitor molecules

2. Material and Methods

In order to obtain a better understanding of the molecular descriptors that define experimental corrosion inhibitive performance, the main objective of this work was to investigate computationally the inhibitor molecular structures and structure parameters using DFT.

2.1. Molecular Reactivity

The molecular geometry, HOMO and LUMO orbitals, and the overall electronic structure of chemical inhibitors were calculated at the DFT level with DMol3using the Materials Studio suite of programs. Structure optimization calculations were performed using a generalized gradient approximation (GGA) function [17, 18] and a hybrid exchange–correlation function (Becke-Lee-Yang-Parr) BLYP [19, 20] with a double numeric plus polarization (DNP) basis set to map the orbital structure of the compound. Frontier molecular orbitals (HOMO and LUMO and the energy gap between them (ΔE) are used to predict the adsorption centres of the inhibitor molecule. According to Koopman's theorem [21-23], the energies of the HOMO and the LUMO orbitals of the inhibitor molecule are related to the ionization potential, (I), and the electron affinity, (A), respectively, by the following Equations:

$$\Delta E = E_{LUMO} - E_{HOMO} \qquad (2.1)$$

$$I = E_{HOMO} \qquad (2.2)$$

$$A = E_{LUMO} \qquad (2.3)$$

Absolute electronegativity, (χ) and global hardness,η , Softness, σ, of the inhibitor molecule are given by Pearson [23].

$$\chi = \frac{1 + A}{2} \qquad (2.4)$$

$$\eta = \frac{I - A}{2} \qquad (2.5)$$

$$\sigma = \frac{1}{\eta} \qquad (2.6)$$

The obtained values of (χ) and (η) are used to calculate the fraction of the electron transferred,ΔN , from the inhibitor to metallic surface as follow [24]:

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2\left(\eta_{Fe} + \eta_{inh}\right)} \qquad (2.7)$$

Using a theoretical value, χ_{Fe}=7 eV and value of η_{Fe}=0 eV for iron according to Pearson's electronegativity scale .[22]

Recently, a new global chemical reactivity parameter has been introduced and known as electrophilicity index ω [9, 10, 25]. It is defined as:

$$\Delta\omega = \frac{\chi^2}{2\eta} \qquad (2.8)$$

Partial atomic charges and atomic Fukui functions are good indicators of selectivity, that is, the region on the molecule on which certain type of reactions is likely to occur [26]. The Fukui functions have been calculated by taking the finite difference approximations from natural population analysis of atoms in all the studied molecules:

$$f^- = (q_N - q_{N-1}) \qquad (2.9)$$

$$f^+ = (q_{N+1} - q_N) \qquad (2.10)$$

$$f^- = \left(\frac{q_{N+1} - q_{N-1}}{2}\right) \qquad (2.11)$$

Here "q" is natural charge of atom in the molecule, that is, the electron density at a point "r" in space around the molecule. The "N" corresponds to the number of electrons in the neutral molecule. "N + 1" corresponds to an anion, with an electron added to the LUMO of the neutral molecule. "N -1" corresponds to a cation, with an electron removed from the HOMO of the neutral molecule. All the calculations were performed at the ground state geometry.

Reactivity of similar atoms of different molecules can also be compared by calculating local softness indices from the Fukui functions and global softness σ by using the following expression:

$$\sigma^- = \left(f^-\right) * \sigma \qquad (2.12)$$

$$\sigma^+ = \left(f^+\right) * \sigma \qquad (2.13)$$

2.2. Molecular Dynamic MD

Molecular dynamics (MD) simulation of the interaction between a single inhibitor molecules and the Fe surface was performed using Forcite quench molecular dynamics [27, 28] to sample different low energy configurations and identify the low energy minima. Calculations were carried out, using the COMPASS [29] (Condensed phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field and the Smart algorithm, in a simulation box 12Å×12Å×24.71Å with periodic boundary conditions to model a representative part of the interface, devoid of arbitrary boundary effects. The box was comprised of the Fe slab and a vacuum layer of 15 Å heights. The Fe crystal was cleaved along the 110 plane and relaxed by minimizing its energy by using molecular mechanics. The temperature was fixed at 298.15 K. Optimized structures of inhibitor molecules and the Fe surface were used for all simulations.

3. Results and Discussion

In our previous studies, we have focused on the experimental study of selected inhibitors Q, HQ, and CA, MA compounds as corrosion inhibitors for mild steel [16]. The classification of these inhibitors according to their inhibition efficiency was found to be HQ > Q, and AB> AM. Table 3.1 and Figure 3.1 summarized the corrosion rates and inhibition efficiency (Inh%) obtained by the addition of Q, HQ, MA and CA at different concentrations on the corrosion of mild steel in 1M HCl solution determined by weight loss at 30 min at 298.15 K.

Quantum chemical calculations were performed to investigate the structural parameters that affect the inhibition efficiency of inhibitors. Geometric and electronic structures of the inhibitors were calculated by the optimization of their energy and bond length. The optimized molecular structures with minimum energies obtained from the DFT calculations are given in Figure 3.2.

The highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) were used to predict the adsorption active site of the inhibitor molecule. According to the frontier molecular orbital theory, [8, 10-12, 24], the formation of a transition state of chemical inhibitor is due to an interaction between E_{HOMO} and E_{LUMO} of the reacting inhibitor. The
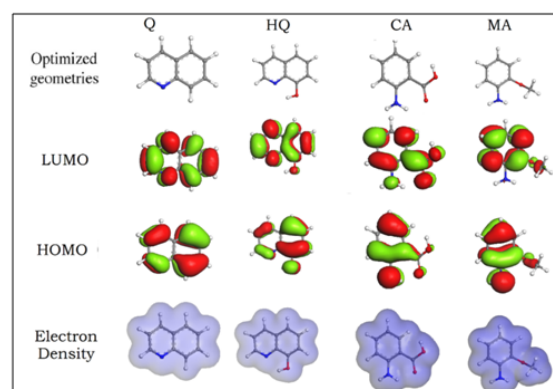
Table 3.1: Corrosion parameters for mild steel in 1 M HCl in the presence of various concentrations of investigated inhibitors at 303.15 k

Conc.	M		A c		H		Q Q	
	$R \times 10^{-5}$ mg cm^{-2} min	Inh%	$R \times 10^{-5}$ mg cm^{-2} min	Inh%	$R \times 10^{-5}$ mg cm^{-2} min	Inh%	$R \times 10^{-5}$ mg cm^{-2} min	Inh%
0	6.5283	/	6.528	/	6.528	/	6.528	/
0.0001	6.4392	1.365	6.464	0.992	6.366	2.492	5.752	11.886
0.0005	6.3346	2.967	6.388	2.15	5.565	14.77	4.568	30.028
0.001	5.8127	10.96	6.335	2.967	5.413	17.08	3.445	47.234
0.0025	5.3536	14.99	6.058	7.199	4.012	38.54	2.172	66.733
0.005	4.8065	26.36	5.858	10.27	1.653	74.68	1.45	77.09
0.0075	3.3916	48.05	5.515	15.52	1.434	78.03	1.234	81.105
0.01	3.1954	51.04	4.717	27.75	1.37	79.02	1.128	82.728
0.015	2.7339	58.12	4.177	36.02	1.124	82.79	0.98	84.998
0.02	2.1045	67.76	3.67	43.78	1.05	83.92	0.975	85.061
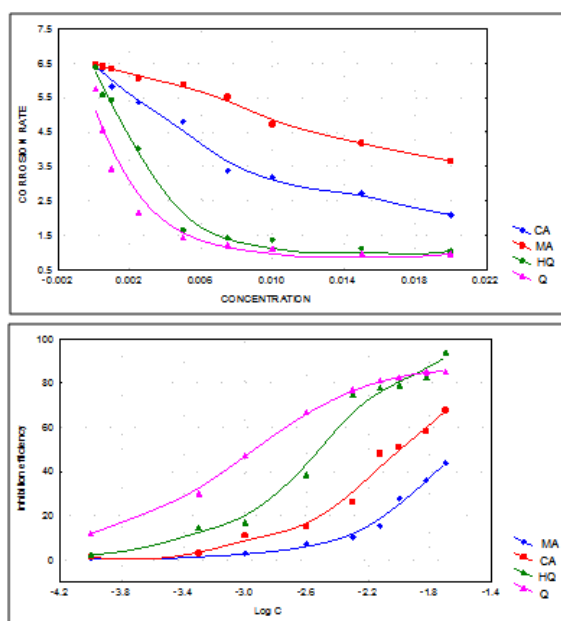
Figure 3.1: Corrosion parameters for mild steel in 1M HCl in the presence of various concentrations of studied inhibitors (a) corrosion rates (b) inhibition efficiencies

Figure 3.2: The obtained optimized molecular structures, HOMO and LUMO of the neutral inhibitor molecules by DFT

energy of HOMO describes the electron donating ability of a molecule and characterizes the tendency of the molecule towards attack by electrophiles. High value of E_{HOMO} indicates a tendency of the molecule to donate electrons to acceptor molecules with low energy molecular orbital or empty electron orbital [8, 12].

However, the LUMO energy characterizes the electron accepting ability and the susceptibility of the molecule towards attack by nucleophiles. Low value of E_{LUMO} indicates an electron accepting ability of an inhibitor molecule (the lowest value the higher the tendency of accepting electrons) [8].The nucleophile centres of the inhibitor molecules are normally heteroatoms with free π-electrons that are readily available for sharing in bond formation [9, 30].

The total electron density (charge distribution) shown in Figure 3.2 reveals that the electron density is saturated all around the molecule. This kind of distribution favored the preferential adsorption of quinoline and phenyl ring on metal surface in two ways: one was the unoccupied d orbitals of Fe atom accepted electrons from in-

hibitor molecule to form coordinate bond. The other was the inhibitor molecule accepted electrons from Fe atom with its anti-bonding orbitals to form back donating.

The calculated energies of the frontier orbitals, presented in Table 3.2, show that the trend of the E_{HOMO} is Q > HQ and AB > AM. The binding ability of the inhibitor to the metal surface increases with increasing of the E_{HOMO} and decreasing of the E_{LUMO} energy values. Therefore, when the two compounds Q and HQ were compared, which have the same skeleton, the calculations show that the compound Q has the highest E_{HOMO} level at -5.405 eV and the lowest E_{LUMO} level at (-1.972 eV) compared to the obtained parameters for HQ (-4.895eV, -2.068 eV). This can explain that the highest inhibition efficiency of Q is due to the increasing energy of the HOMO and the decreasing energy of the LUMO.

The gap energy between the frontier orbitals ΔE-($_{HOMO-LUMO}$) (Equation 2.1), is another essential factor that defines the reactivity of inhibitor molecules towards adsorption on metal surfaces [21]. Generally, large values of the energy gap (ΔE) imply high electronic stability and then, low reactivity, whoever, the low values imply that it will be easier to remove an electron from the HOMO orbital to LUMO, which can result in good inhibition efficiency (the lower the value of ΔE, the higher the stability for the formed complex), since the energy to remove an electron from the last occupied orbital will be minimized [31]. The value of ΔE gap for Q, HQ, AM and AB are -3.433, -2.827, -3.944 and -2.867eV, respectively as presented in Table 3.2. Therefore, the energy band gap (ΔE) were found to be in order of MA> CA, this result is in agreement with experimental data. Thus, it is concluded that the energy band gap (ΔE), is a good quantity to correlate with experimental inhibition efficiencies of the phenyl ring based compounds inhibitors under investigation.

The dipole moment μ provides information on the polarity of the whole molecule [31, 32]. The total dipole moment reflects the global polarity of a molecule. High dipole moment probably gives rise to high chemical reactivity [28]. It was reported previously by some researchers that higher values of dipole moment (μ) are responsible for higher inhibition efficiency [31]. The values of the dipole moment displayed in Table 3.2, show that CA have the highest dipole moment value (5.3856 D), which will increase its molecular reactivity, leading to stronger adsorption onto the mild steel surface compared to the adsorption of AM. Similarly, the HQ molecules have higher dipole momentum (2.6753 D) than Q molecules (2.0671 D).

The electronegativity indicates the molecular capability of accepting electrons. Since good inhibitors are the inhibitors have ability to donate electrons to the metal surface, it is expected the electronegativity values to decrease with the increase of inhibition efficiencies [32]. The values of χ of the calculated molecules are presented in Table 3.2. The trend in the χ values for the inhibitors show that HQ molecules have the lowest value of electronegativity (5.315 eV) than Q molecules (6.391 eV) which is probably due to the presence the electron withdrawing effect (-I) of the hydroxyl group OH [32]. This effect increases its adsorption on the mild steel. Another important parameter of molecular reactivity is fraction of electrons transferred. When the value of the fraction of electrons transferred (ΔN) below 3.6,the molecule will have tendency to donate electrons to the mild steel surface [33]. Therefore, the higher its value the better the corrosion inhibitive efficiency [5]. The obtained values of ΔN reported in Table 3.2; show that the HQ molecules have the higher value of ΔN (0.138695) than Q molecules (0.068907). The (ω) is proposed as a measure of the electrophilic power of a molecule and there obtained values reported in Table 2. Generally, a small value of elecrophilicity describes a good nucleophile while a high value of electrophilicity(ω) defines a good electrophile. The electrophilicity is a measure of reactivity that quantitatively classifies the global electrophilic nature of a molecule within a reactive scale. In addition, high ionization energy (I) indicates high stability, while low ionization energy indicates high reactivity of the atoms and molecules [34]. Therefore, the corrosion inhibition of the molecule will be high.

Generally, the molecule with lower value of hardness (hence highest value of softness) is expected to have the highest inhibition efficiency [11]. It is clear from the calculation that CA molecule has the lowest hardness and the highest softness than MA, which follow the same trend as obtained experimentally.Table 3.2 presents the hardness (η) and softness(σ) values obtained for the studied in-

**Table 3.2:** The calculated quantum chemical parameters of the investigated inhibitors

Parameters quantities	Q	HQ	MA	CA
E_{HOMO}	-5.405	-4.895	-4.858	-5.111
E_{LOMO}	-1.972	-2.068	-0.914	-2.244
energy band gap (ΔE)	-3.433	-2.827	-3.944	-2.867
Ionization potential l(I)	5.405	4.895	4.858	5.111
Electroaffinity (A)	1.972	2.068	0.914	2.244
Electronegativity (χ)	6.391	5.929	5.315	6.233
Global hardness(η)	4.419	3.861	4.401	3.989
global softness (σ)	0.226296	0.259	0.227221	0.250689
Electrons transferred fraction (ΔN)	0.068907	0.138695	0.191434	0.096139
electrophilicity(ω)	4.62151	4.552323	3.18115	4.8696
dipole moment (μ) Debye	2.0671	2.6753	1.4631	5.3856

hibitor molecules. The hardness value of the HQ molecule is smaller than this of the Q molecules. This result does not supports the experimental observation (the Q molecule is more efficient inhibitors than the HQ molecule).

It can be concluded that, the E_{HOMO} and E_{LUMO} orbits are the most important parameter that can explain the experimental values of inhibition characteristic of the studied molecules. These results can be interpreted in terms of the electronic nature of the substituent, as the electron releasing ability (+I) of the methoxy group in MA molecules which enhances the electron density in the phenyl ring leading to better electron donating ability of AM compared to AB. On the other hand, the electron withdrawing effect (I) of the OH in HQ results in electron deficiency in the pyridine ring enhancing the electron accepting ability of HQ.
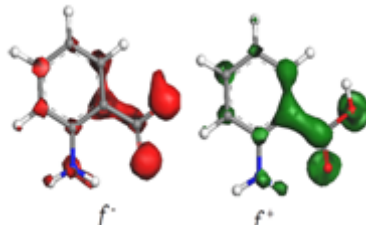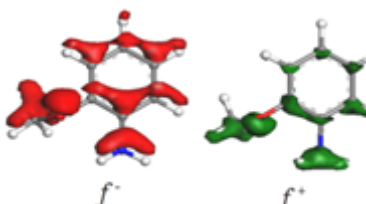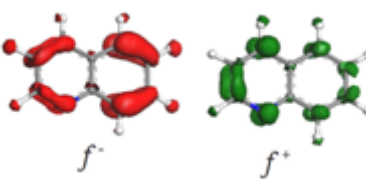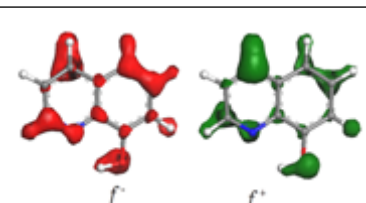
The Fukui functions provide information about the molecule sites that are probable to be involved in electrophilic attack or the sites are likely to be involved in nucleophilic attack [35]. The preferred site for nucleophilic attack is the atom or group of atoms in the molecule where the value of f^+ is the highest, while the site for electrophilic attack is where the value of f^- is the highest. Figure 3.3 shows the Fukui function for the studied inhibitors. For the simplest transfer of electrons, adsorption could occur at the part of the molecule, where local softness (s) has the highest value. A high value of s+ indicates high nucleophilicity and a high value of s indicates high electrophilicity [35].

An analysis of Fukui functions For quinoline based inhibitors that given in Table 3.3, shows that, the
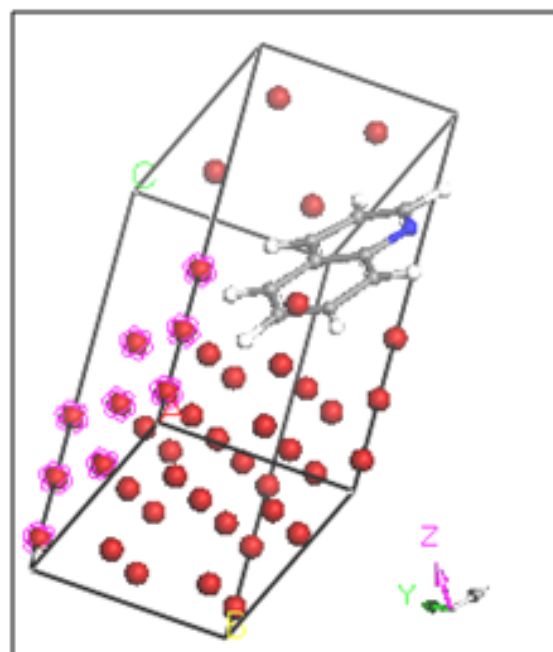
Figure 3.3: Outputs and descriptors calculated by the Monte Carlo simulation for the lowest adsorption configurations of quinoline (Q) on Fe (110) surface

π- system are preferred sites for electrophilic attack and also the nucleophilic attack, as these sites have higher values of Fukui function ($f-$) and ($f+$). It's clear that the OH group in HQ molecules is only acts as electrophile ($f- = 0.128$), and this can be explain unreactively of this group to enhance the corrosion inhibition. However, the analysis of Fukui functions for aniline based inhibitors showed that the NH_2 group is preferred

Table 3.3: Condensed Fukui Fukui f− and f+ function and local softness σ $^-$ and σ$^+$

atoms	f$^-$	f$_+$	σ $^-$	σ $^+$	
-NH$_2$	0.163	0.053	0.04086	0.01329	
C of carboxyl	0.108	0.145	0.02707	0.03635	
O of carboxyl	0.053	0.105	0.01329	0.02632	
O of hydroxyl	0.041	0.050	0.01028	0.01253	
C of phenyl	0.037	0.095	0.00928	0.02382	
ring	0.087	0.093	0.02181	0.02331	

atoms	f$^-$	f$^+$	σ $^-$	σ $^+$	
-NH$_2$	0.176	0.029	0.03999	0.00659	
O of methoxy	0.028	0.022	0.00636	0.005	
C of phenyl	0.073	0.150	0.01659	0.03408	
	0.103	0.102	0.0234	0.02318	
ring	0.083	0.156	0.01886	0.03545	

atoms	f$^-$	f$^+$	σ $^-$	σ $^+$	
-N=	0.075	0.105	0.01697	0.02376	
C of phenyl	0.079	0.057	0.01788	0.0129	
ring	0.081	0.059	0.01833	0.01335	

atoms	f$^-$	f$^+$	σ $^-$	σ $^+$	
-N=	0.032	0.100	0.00829	0.0259	
O of hydroxyl	0.128	0.056	0.03315	0.0145	
C of phenyl	0.093	0.104	0.02409	0.02694	
ring	0.067	0.054	0.01735	0.01399	

Table 3.4: Outputs and descriptors calculated by the Monte Carlo adsorption simulation on Fe (110)

Structures	Total energy	Adsorption energy	Rigid adsorption energy	Deformation energy	dE$_{ad}$/d$_{Ni}$
Q	26.426	-49.4001	-46.855	-2.546	-49.40
HQ	23.335	-64.593	-67.894	3.301	-64.59
MA	-42.3462	-57.201	-62.587	5.386	-57.201
CA	-118.559	-96.0085	-113.271	17.263	-96.0085

sites for electrophilic attack, as these sites have higher values of Fukui function ($f-$). An analysis of Fukui functions for quinoline based inhibitors that given in Tables 3, shows that and are. The atoms C_6, C_{16}, and O_{11} carboxyl COOH groups and are π- system most susceptible sites for nucleophilic attack since these sites have highest values of Fukui function ($f+$).

To describe the interaction between metal and inhibitor, the molecular dynamics simulation has been used. Because it provides some important parameters as: total energy, rigid adsorption energy (the released or absorbed energy in kcal/mol when the unrelaxed atom or group of atoms were adsorbed on the mild steel surface), deformation energy (is the released energy when the adsorbed atom or group of atoms are relaxed on the mild steel surface), and adsorption energy (the sum of rigid adsorption energy and deformation energy, which is defined as adsorption energy for the adsorbate components) [34, 36, 37] .

In this study the lowest energy for the adsorption are presented in Table 3.4 and Figure 3.3). The quantity (dEads/dNi) described in Table 4 represents the energy of mild steel-adsorbate configurations where one of the adsorbate components have been removed. The data in this table represents the most stable low energy configuration for the adsorption of selected compounds on Fe (110) surface. All the investigated inhibitors adsorbed nearly parallel to the Fe (110) surface, and they adsorb on the metal surface through the nitrogen and oxygen atoms as well as the six-membered aromatic rings.

In O-substituted anilines the carboxyl group inhibits iron corrosion due to increase of the delocalization of electron density in the molecule, which makes the molecule more stable and better inhibition. methoxy anilines give protection because of the presence of oxygen in addition to nitrogen in these molecules, which enhance the adsorption power to iron surface[6].

O-substituted anilines may adsorb on the iron surface as (i) a neutral molecule via chemisorption mechanism [15, 38] involving the sharing of electrons between the nitrogen atom and iron, (ii) through π-electron interactions between the pyridine or benzene ring of the molecule and the metal surface, (iii) through the cationic form with positively charges part of the molecule (ammonium-NH3_) oriented toward negatively charges iron surface [15].The nitrogen atoms present in the molecules can be easily protonated in an acidic solution and convert into quaternary compounds. These protonated species adsorb onto the cathodic sites of the mild steel and decrease the evolution of hydrogen. The adsorption on the anodic site occurs through π-electrons of triazole, and phenyl rings and lone pair of electrons of nitrogen and sulfur atoms present in both the inhibitors which decrease the anodic dissolution of mild steel [31]. It was assumed by Ebenso [11] that due to the planar geometry of the inhibitor, the molecular adsorption most likely occurs in such a manner that the metal surface and the molecular plane are parallel to each other and that in this conformation, the interaction is dominated by the donation and back donation between the molecule and the metal surface [34]. However, the reverse is true, i.e., if the inhibitor species is not planar, then a direct relationship will be obtained between the %Inh values and the hardness values.

4. Conclusion

From the obtained results and by using the DFT calculations, the inhibition efficiency of some N-containing organic compounds is investigated that leads to the following conclusions:

1. Quantum chemical results of quinolines and anilines showed a higher value of E_{HOMO}, a lower value of E_{LUMO}, and a smaller value of ΔE, indicating that both inhibitors are good at inhibiting corrosion of mild steel in a 1MHCl solution.

2. The studied inhibitors will adsorb on the iron surface as a neutral molecule, through π-electron interactions and/or through the cationic form with positively charges part of the molecule (ammonium-NH3_).

3. When we compared the two compounds MA and CA, which have the same skeleton, the calculations show that the compound CA has the highest HOMO level and the lowest LUMO level compared to obtained parameters for MA. This can explain that the highest inhibition efficiency of CA is due to the increasing energy of the HOMO and the decreasing energy of the LUMO.

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