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Theoretical study on the corrosion inhibitor potential of moxifloxacin for API 5L X-52 steel in acidic environment

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Abstract. Density functional theory (DFT) is used to obtain the energy of an electron in the ground state which in turn enables the prediction of the inhibition efficiency of a molecule in the corrosion of metals. The electronic and molecular structure relationship of moxifloxacin acting as corrosion inhibitor on the corrosion of API 5L X-52 steel in acidic media was studied using DFT with B3LYP basis set. Quantum chemical parameters calculated from the Density functional theory model were as follows; E_{HOMO} , E_{LUMO} , electronegativity χ , global hardness η , electrophilicity index ω , the number of electrons transferred from the inhibitor molecule to the metal ΔN and energy of the back-donation ($\Delta E_{back-donation}$). The outcome of the analysis suggests that the studied molecule functions as an effective additive that slows down the corrosion process, and the data corroborates experimental results earlier reported.

1. Introduction

Corrosion of metals commonly occur in most chemical manufacturing, construction and oil and gas industries. Corrosion is the destruction of a material caused by the environment in which the material resides [1]. The industrial cost involved in preventing the problem of corrosion is high and so there is considerable drive from industry to find cheap and effective additives to control the problems of corrosion [2]. The chemical components in medicinal drugs act as inhibitive substances in corrosion prevention. Several reports on the use of pharmaceutical drugs as corrosion inhibitor has been documented using experimental measurements such as gravimetric and electrochemical methods [3-15].

As a contribution to the current interest, the present study aims at broadening the application of Density Functional Theory (DFT) for metallic corrosion inhibition. Moxifloxacin is utilized for the study as it presents the basic characteristic of an effective corrosion inhibitor, namely the presence of nitrogen and oxygen, and in addition is economically friendly and cheap. The reactivity of the molecule is affected by the ground state spatial arrangement of the molecule, and the shape and structure of both its highest occupied molecular orbital (HOMO) and its lowest unoccupied molecular orbital (LUMO).

The inhibition efficiency of the studied compound was previously reported [1, 2] using potentiodynamic polarization measurements, gravimetric measurements and electrochemical impedance spectroscopy. Theoretical chemical parameters to be calculated include energy of highest occupied molecular orbital E_{HOMO} , energy of the lowest unoccupied molecular orbital E_{LUMO} , electronegativity χ , ionization energy I , electron affinity A , global hardness η , global softness σ , the



number of electrons transferred from the inhibitor molecule to the atom of the metal ΔN , energy of back-donation $\Delta E_{back-donation}$ and electrophilicity index ω .

2. Methodology

One of the computational chemistry tools that offer the basics for interacting many chemical concepts employed in diverse fields of chemistry is DFT. To investigate the consistency between theoretical and experimental data, quantum chemical calculations were carried out on a completely optimized geometrical structure of the compound. The optimization was performed by B3LYP functional at level of DFT. The density functional theory is regarded as an important method to examine the interactions at the inhibitor/surface interface. The chemical structure of moxifloxacin and the result of the geometry optimization of the studied compound is illustrated in Figure 1 and Figure 2 respectively.

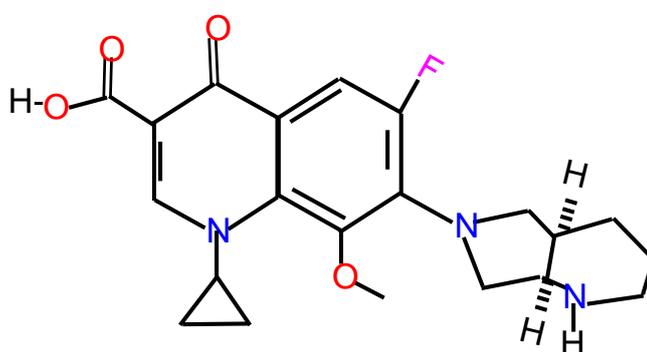


Figure 1. Chemical structure of moxifloxacin.

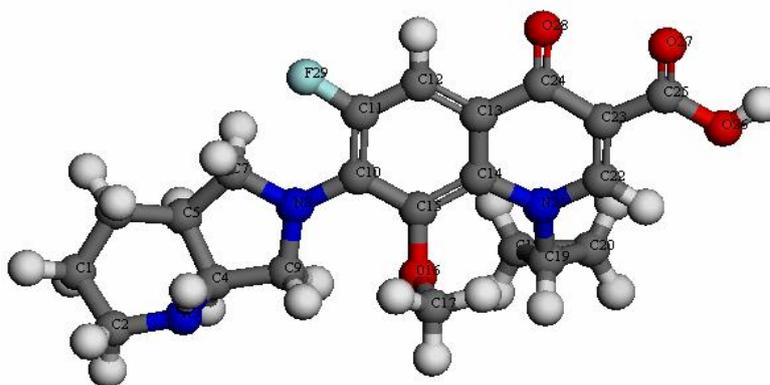


Figure 2. Optimized structure of moxifloxacin.

2.1. Theoretical and computational details

Parr, Donnelly, Levy and Palke [14, 16] related the first derivative of the electronic energy with respect to the number of electrons to the chemical potential μ . The mean value of ionization energy I and electron affinity A as well as the negative of electronegativity χ are given in (1) as finite difference version of chemical potential [9].

$$-\mu = \chi = \frac{\partial E}{\partial N_{ele}} \approx \frac{(I + A)}{2} \quad (1)$$

The principle of Koopmans theorem explains how E_{HOMO} and E_{LUMO} of the molecule are associated to I and A respectively. The principle considers the negative of HOMO energy as I and the negative of LUMO energy as A [9, 17]. The electronegativity χ is also expressed in terms of orbital energy as shown in (2).

$$\chi = -(E_{HOMO} + E_{LUMO})/2 \quad (2)$$

The global hardness η (3) can be expressed as the second derivative of energy with respect to the number of electrons and may also be estimated from the values of the ionization energy and electron affinity of the studied compound.

$$\eta = \frac{1}{2}(\partial^2 E / \partial^2 N_{ele}) \approx (I - A)/2 \quad (3)$$

The reciprocal of global hardness indicates global softness σ shown in (4).

$$\sigma = 1/\eta \approx 2/(I - A) \quad (4)$$

Equation (5) defines electrophilicity index ω as a degree of electrophilic strength of a molecule [15, 17].

$$\omega = \chi^2/2\eta = (I + A)^2/4(I - A) \quad (5)$$

The number of electrons transferred ΔN can be computed based on Pearson theory [18], as expressed in (6).

$$\Delta N = \chi_{Fe} - \chi_{inh} / 2 \sum \eta_{Fe} + \eta_{inh} \quad (6)$$

The electronegativity of iron and the inhibitor molecule are represented as χ_{Fe} and χ_{inh} respectively, while η_{Fe} is the global hardness for iron atom and η_{inh} the global hardness for the inhibitor molecule. Theoretically, χ_{Fe} and η_{Fe} are assigned the values 7.0 eV and 0 respectively. The power of a molecule to pull to itself electrons in a covalent bond is identified in the electronegativity χ and global hardness η parameters [15, 17]. Equation (6) shows that the number of electrons transferred is related to the differences in χ and the sum of the hardness parameter [9].

Gomez et al. [17] developed a framework of charge transfer for donation and back donation of charges. Electron back-donation as illustrated in (7) is a process that explains the interaction between the metal surface and inhibitor molecules.

$$\Delta E_{Back-donation} = -\eta/4 \quad (7)$$

When the energy of the back-donation is less than zero ($\Delta E_{Back-donation} < 0$), and the hardness is greater zero $\eta > 0$, it implies that there is transfer of charge to the molecule which is succeeded by back-donation to unoccupied d orbital of the metal atom and such behaviour would reflect a good inhibition process [9, 15, 17]. Equation (8) and (9) give expressions for electron donating ω^- and electron accepting ω^+ powers respectively.

$$\omega^- = (3I + A)^2 / 16(I - A) \quad (8)$$

$$\omega^+ = (I + 3A)^2 / 16(I - A) \quad (9)$$

A large ω^+ value reflects an enhanced capacity of the molecule to accept charge. On the other hand, a small value of ω^- is indicative of a good electron donor. Equation (10) can be used to match together ω^- and ω^+ ; the electron donating and electron accepting power.

$$\Delta\omega^\pm = \omega^+ - (-\omega^-) = \omega^+ + \omega^- \quad (10)$$

3. Results and Discussion

Chemical reactivity as described by the Frontier Molecular Orbital Theory (FMOT), has it that the interaction between the inhibitor molecule and the metal occurs through the transfer of the electron from the HOMO of the inhibitor to the vacant d-orbital of a metal (LUMO) [13].

3.1. Ionization energy

Chemical reactivity of molecules and atoms can be described from a knowledge of the ionization energy I . High stability and chemical hardness is suggestive of a high ionization energy and vice versa [9, 15]. The ionization energy value of the studied molecule has been presented in Table 1. It shows the molecule having a low ionization energy value which indicates high inhibition efficiency of the molecule. Generally, a small ionization energy of the range of -0.1 to 10 eV has been reported by [18-23], while I above 10 eV is considered a large type of ionization energy as reported by [24].

3.2. Electronegativity

As earlier mentioned, the absolute electronegativity depicts a molecule's capacity to pull on the electrons in a covalent bond. Table 1 shows the calculated value of electronegativity of the molecule which can quickly reach equalization, expecting realistic inhibition efficiency according to Sanderson's electronegativity equalization principle [17].

Table 1. Calculated quantum chemical parameters of the studied compound.

E_{HOMO} (eV)	E_{LUMO} (eV)	I (eV)	A (eV)	χ (eV)	η (eV)	Σ (eV ⁻¹)	ω^- (eV)	ω^+ (eV)	$\Delta\omega^\pm$ (eV)	ΔN (e)	$\Delta E_{Back-donation}$
-4.613	-2.173	4.613	2.173	3.393	1.220	0.819	6.567	3.174	9.741	1.478	-0.303

3.3. Hardness and Softness

Another quantum chemical parameter that measures molecular reactivity and stability is global hardness η . It is a signifier of the resistance towards the polarization of the electron cloud of the molecules, atoms or ions when these systems undergo a small perturbation. Hard molecules have a large energy gap value ($\Delta E_{LUMO-E_{HOMO}}$) greater than 10 eV [24] whereas a small energy gap of within -0.01-10 eV is attributed to a soft molecule [7, 18-23]. Our study reveals that the inhibitor molecule can be considered a soft molecule implying that it is reactive as it readily gives electrons to the metal. This means that the studied molecule would offer a good inhibition performance.

3.4. Number of electrons transferred

The calculated value for the sum of electrons transferred is determined using (6) and is listed in Table 1. Several authors have opined that if the number of electrons transferred is less than 3.6 ($\Delta N < 3.6$), such inhibitor has a good electron donating ability to the empty d-block orbital [9, 13, 15]. It was revealed from the study that the molecule has value of 1.478 as the number of electrons transferred, meaning it would be expected to function well as a good corrosion inhibitor. Ikpi et al. [1] confirmed the efficacy of this molecule using electrochemical corrosion test methods.

3.5. Back-donation

Table 1 also illustrates the value of $\Delta E_{Back-donation}$ calculated from (7). During charge transfer process, back donation charges also occur, which influence the bonding interaction between the inhibitor molecule and the surface of the metal. According to Gomez et al. [17], when $\Delta E_{back-donation}$ value of inhibitor is less than zero and the value of hardness of the same inhibitor is greater than zero, it signifies that the molecule is favoured energetically. The results therefore correspond with the theory of Gomez et al. [17].

3.6. Electrophilicity index

Electrophilicity index ω measures the stabilization in energy after a system accepts further amount of electron charge from the environment [15]. The electrophilicity index ω is further defined in (5), (8), (9) and (10). The net electrophilicity index is given as $\Delta\omega^\pm$, where ω^- represents the electron donating power and ω^+ the electron accepting power. Their values are presented in Table 1. The value of ω^- makes the inhibitor an excellent electron donor whereas ω^+ value makes the studied compound capable of accepting charge.

3.7. Mulliken atomic charge

The diagrams of HOMO and LUMO of the investigated compound are shown in Figure 3. The HOMO reflects dense electron cloud while LUMO shows lack of electron dense cloud. To explain the mechanism of inhibition of the molecule we have to employ mulliken atomic charges (Table 2).

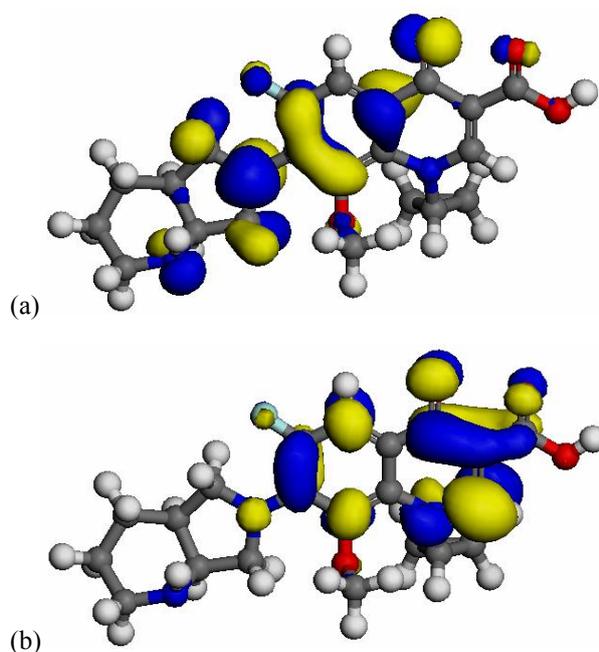


Figure 3. Frontier molecular orbital diagrams of moxifloxacin, (a) HOMO and (b) LUMO.

The ease at which an atom donates electrons to the unoccupied d-orbital of the metal is dependent on the atomic charge of the constituent atoms of the molecule that is more negative. Table 2 reveals that oxygen and nitrogen atoms exhibit more negative charges. These atoms can provide electrons to the surface of the metal thereby forming a coordinate complex as shown in Figure 4. Nitrogen and

Table 2. Mulliken atomic charges on moxifloxacin.

Atom	Charge	Atom	Charge	Atom	Charge
C1	-0.255	C10	0.138	C19	-0.273
C2	-0.140	C11	0.328	C20	0.096
N3	-0.458	C12	-0.103	N21	-0.354
C4	0.036	C13	-0.065	C22	-0.009
C5	-0.091	C14	0.113	C23	0.027
C6	-0.254	C15	0.239	C24	0.292
C7	-0.054	O16	-0.570	C25	0.532
N8	-0.357	C17	-0.156	O26	-0.678
C9	-0.059	C18	-0.239	O27	-0.387

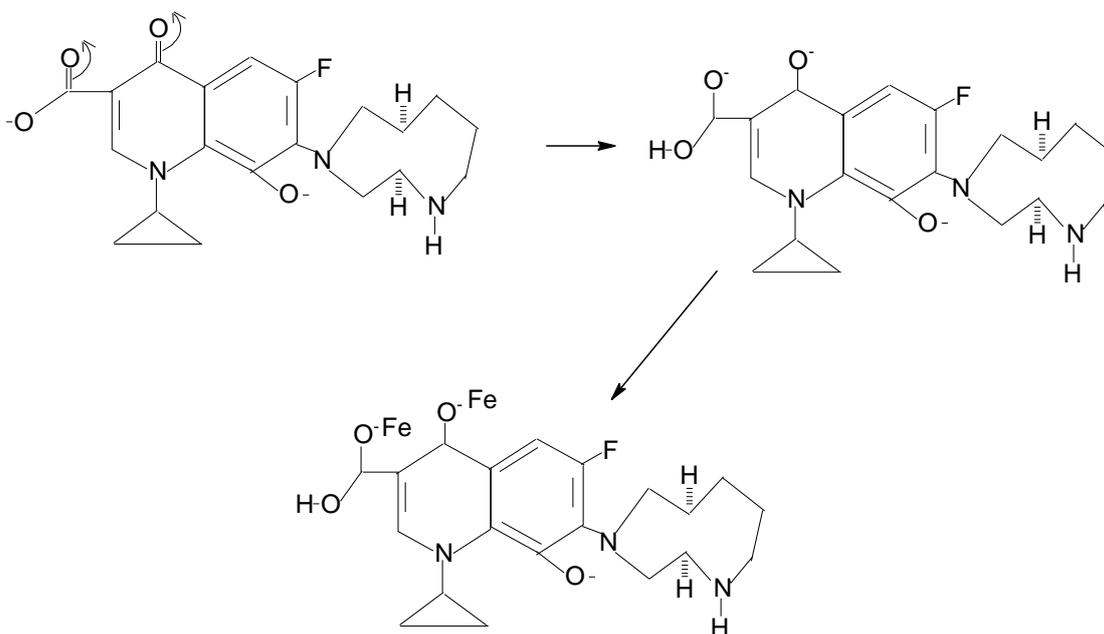


Figure 4. Corrosion inhibition mechanism of moxifloxacin on API 5L X-52 steel in 2 M HCl.

oxygen atoms are heteroatoms that have lone pairs of electron which can easily donate electrons to the empty d-orbital of the metal, enhancing adsorption onto the metal surface, facilitating inhibition of corrosion of the metal. The results reveal that adsorption of the studied molecule can easily occur at N3, N8, O16, N21, O26 and O27 atoms.

4. Conclusion

Density functional theory (DFT) has been used to study the inhibitory properties of moxifloxacin at B3LYP/6-31G basis set. The calculated quantum chemical parameters that describe the electronic activity of the investigated compound is in agreement with the inhibition efficiency results of this molecule earlier reported by [1, 2]. The potentially good inhibition efficiency of the molecule reflects in the value of E_{HOMO} and the low value of the energy gap obtained from the computational analysis.

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