Research Article

Quantum Chemical Study on the Corrosion Inhibition of Some Oxadiazoles

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Quantum chemical calculations based on DFT method were performed on three nitrogen-bearing heterocyclic compounds used as corrosion inhibitors for the mild steel in acid media to determine the relationship between the molecular structure of inhibitors and inhibition efficiency. The structural parameters, such as energy and distribution of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), the charge distribution of the studied inhibitors, the absolute electronegativity (χ) values, and the fraction of electrons (ΔN) transfer from inhibitors to mild steel were also calculated and correlated with inhibition efficiencies. The results showed that the inhibition efficiency of inhibitors increased with the increase in energy of HOMO and decrease in energy gap of frontier molecular orbital, and the areas containing N and O atoms are most possible sites for bonding the steel surface by donating electrons to the mild steel.

1. Introduction

Acid solutions are widely used in industry, for example, chemical cleaning, descaling, and pickling, which leads to corrosive attack. Therefore, the consumption of inhibitors to reduce corrosion has increased in recent years [1–4]. The majority of the well-known inhibitors are organic compounds containing heteroatoms, such as oxygen, nitrogen, or sulphur, and multiple bonds, which allow an adsorption on the metal surface [2, 3]. In any case, adsorption is generally over the metal surface forming an adsorption layer that functions as a barrier protecting the metal from the corrosion [2, 3].

In order to evaluate compounds as corrosion inhibitors and to design novel inhibitors, much more research works were concentrated on the studies of the relationship between structural characteristics of the organic compounds and their inhibiting effects [5–8]. It had been suggested that the most effective factors for the inhibiting effects are the electronegative atoms (such as, N, S, P, and O) [5, 6], the unsaturated bonds (such as double bonds or triple bonds) [7, 8], and the plane conjugated systems including all kinds of aromatic cycles, of which they can offer special active electrons or vacant orbital to donate or accept electrons. Heterocyclic compounds, kind of effective inhibitors [6–9],

have at least two factors within their structures, which is the reason of their effective inhibiting. The planarity (π) and the lonely electron pairs in the heteroatoms are important features that determine the adsorption of these molecules on the metallic surface by transferring electrons from the organic compounds to the metal and forming a coordinate covalent bond during the chemical adsorption [6, 7].

Theoretical chemistry has been used recently to explain the mechanism of corrosion inhibition, such as quantum chemical calculations [10–13]. Quantum chemical calculations have been proved to be a very powerful tool for studying the mechanism [14–16]. The objective of this work is to present a theoretical study on electronic and molecular structures of three heterocyclic compounds (Figure 1) and to determine relationship between molecular structure of the compounds and inhibition efficiency. The structural parameters, such as energy and distribution of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), the charge distribution of the studied inhibitors, the absolute electronegativity (χ) values, and the fraction of electrons (ΔN) transfer from inhibitors to mild steel were also calculated and correlated with inhibition efficiencies. This work has great significance for the investigation of inhibition mechanism in theory. And it will be helpful

FIGURE 1: The chemical structure of the investigated compounds.

to provide reference for screening corrosion inhibitors before the experiment.

2. Theory and Computational Details

Density functional theory (DFT) methods were used in this study. These methods have become very popular in recent years because they can reach exactitude similar to other methods in less time and they are less expensive from the computational point of view. In agreement with the DFT results, energy of the fundamental state of a polyelectronic system can be expressed through the total electronic density, and, in fact, the use of electronic density instead of wave function for calculating the energy constitutes the fundamental base of DFT [16]. All the calculations were done by GAUSSIAN 03W software [17], using the B3LYP functional [18, 19] and a 6-31G* basis set [19]. The B3LYP, a version of DFT method, uses Becke's three-parameter functional (B3) and includes a mixture of HF with DFT exchange terms associated with the gradient corrected correlation functional of Lee, Yang, and Parr (LYP) [18, 19]. This approach is shown to yield favorable geometries for a wide variety of systems. This basis set gives good geometry optimizations.

3. Results

Table 1 presents the calculated parameters for the three selected compounds. The measured average inhibition efficiencies (%) of these three heterocyclic compounds were also listed in the table [20].

The relationship between corrosion inhibition efficiency and HOMO energy levels for these three compounds is plotted in Figure 2. As clearly seen in the figure, the inhibition efficiency increased with the E_{HOMO} level rising. In Figure 3, inhibition efficiency is plotted against the LUMO energy, showing that the inhibition efficiency reduced with the E_{LUMO} level increase. The relationship between the inhibition efficiency and the energy gap ($E_{\text{LUMO}} - E_{\text{HOMO}}$) is negative (Figure 4).

The frontier molecule orbital density distributions of three *n*-POXs were presented in Figure 5. As seen from the figure, the distributions of HOMO and LUMO were mainly average around the whole compound structure, but the population densities of three compounds' frontier orbitals have a more obvious difference. 2-POX and 3-POX have higher and more uniform population densities than 4-POX.

The Mulliken charge populations of the three *n*-POXs were also calculated (Figure 6). It can be seen that the area of

FIGURE 2: The relations between corrosion IE and E_{HOMO} of *n*-POX. FIGURE 3: The relations between corrosion IE and E_{LUMO} of *n*-POX.

nitrogen and oxygen atoms charged a large electron density and might form adsorption active centers.

4. Discussion

4.1. Correlation between MO Energy Level and Inhibition Efficiency. Frontier orbital theory is useful in predicting adsorption centers of the inhibitor molecules responsible for the interaction with surface metal atoms [5, 15]. Terms involving the frontier MO could provide dominative contribution, because of the inverse dependence of stabilization energy on orbital energy difference [5]. Moreover, the gap between the HOMO and LUMO energy levels of the molecules was another important factor that should be considered. Reportedly, excellent corrosion inhibitors are usually those organic compounds which not only offer electrons to unoccupied orbital of the metal, but also accept free electrons from the metal [5, 11].

According to Gece and Bilgiç [20], when the position of N atoms was changing, the corrosion inhibition efficiency changed. The quantum chemistry calculation in this study revealed that the HOMO energy level of 3-POX was boosted significantly while the energy gap dropped sharply. The linear

TABLE 1: Molecular property of *n*-POXs calculated with B3LYP/6-31G*.

Compound	E_{HOMO} [eV]	E_{LUMO} [eV]	$(E_{\text{LUMO}} - E_{\text{HOMO}})$ [eV]	Dipole moment (Deby)	Inhibition efficiency η (%)
2-POX	-7.33	-2.53	4.80	0.431	79
3-POX	-7.15	-2.58	4.57	0.466	84
4-POX	-7.37	-2.48	4.89	0.423	68

FIGURE 4: The relations between corrosion IE and HOMO-LUMO energy gaps of *n*-POX.

correlation between MO energy level and the corrosion inhibition efficiency of the *n*-POXs (Figures 2, 3, and 4) proved that the higher the HOMO energy of the inhibitor, the greater the trend of offering electrons to unoccupied d orbital of the metal and the higher the corrosion inhibition efficiency for iron in HCl acid solutions; in addition, the lower the LUMO energy, the easier the acceptance of electrons from metal surface, as the HOMO-LUMO energy gap decreased and the efficiency of inhibitor improved.

The number of transferred electrons (ΔN) was also calculated depending on the quantum chemical method [21, 22]:

$$\Delta N = \frac{(\chi_{\text{Fe}} - \chi_{\text{inh}})}{[2(\eta_{\text{Fe}} + \eta_{\text{inh}})]}, \quad (1)$$

where χ_{Fe} and χ_{inh} denote the absolute electronegativity of iron and the inhibitor molecule, respectively; η_{Fe} and η_{inh} denote the absolute hardness of iron and the inhibitor molecule, respectively.

These quantities are related to electron affinity (*A*) and ionization potential (*I*):

$$\chi = \frac{(I + A)}{2}, \quad (2)$$

$$\eta = \frac{(I - A)}{2}, \quad (3)$$

where *I* and *A* are related in turn to E_{HOMO} and E_{LUMO} :

$$I = -E_{\text{HOMO}}, \quad (4)$$

$$A = -E_{\text{LUMO}}. \quad (5)$$

Values of χ and η were calculated by using the values of *I* and *A* obtained from quantum chemical calculation. Using

a theoretical χ value of 7 eV/mol and η value of 0 eV/mol for iron atom [21], ΔN , the fraction of electrons transferred from inhibitor to the iron molecule, was calculated. And the plot of inhibition efficiency versus ΔN (Figure 7) clearly shows that the inhibition efficiency increased with the ΔN increase. According to other reports [21, 22], values of ΔN showed that inhibition effect resulted from electrons donation. Agreeing with Lukovits's study [22], if $\Delta N < 3.6$, the inhibition efficiency increased with increasing electron-donating ability at the metal surface. In this study, the three *n*-POXs were the donors of electrons, and the iron surface was the acceptor. The compounds were bound to the metal surface and thus formed inhibition adsorption layer against corrosion. 2-POX had the highest inhibition efficiency because it had the highest HOMO energy and ΔN values, and it had the greatest ability of offering electrons, and 2-POX had the lowest inhibition efficiency, for vice versa.

4.2. Correlation between Electronic Density and Inhibition Efficiency. Frontier orbital energy level indicates the tendency of bonding to the metal surface. Further study on formation of chelating centers in an inhibitor requires the information of spatial distribution of electronic density of the compound molecules [5].

The structure of the molecules can affect the adsorption by influencing the electron density at the functional group. Generally, electrophiles attack the molecules at negative charged sites. As seen from Figure 6, the electron density focused on N atoms. The regions of highest electron density are generally the sites which electrophiles attacked. So N and O atoms were the active center, which had the strongest ability of bonding to the metal surface. On the other side, HOMO (Figure 5) was mainly distributed on the areas containing nitrogen and oxygen atoms. Thus, the areas containing N and O atoms were probably the primary sites of the bonding. And inhibition efficiency was enhanced by increase in HOMO energy and electron density. It is concluded that the region of active centers transforming electrons from N atoms to iron surface. The electron configuration of iron is [Ar] 4s²3d⁶; the 3d orbitals are not fully filled with electrons. N and O atoms have lonely electron pairs that are important for bonding unfilled 3d orbitals of iron atom and determining the adsorption of the molecules on the metal surface. 3-POX had the highest inhibition efficiency among the *n*-POX, which resulted from the geometry change that led to HOMO energy increase and electron density distribution in the molecule. On the contrary, 4-POX had the lowest inhibition efficiency because of the lowest and the most uneven population density of HOMO.

FIGURE 5: The frontier molecule orbital density distributions of three *n*-POXs: HOMO (left) and LUMO (right).

FIGURE 6: The Mulliken charge population of three *n*-POXs.

FIGURE 7: The relations between corrosion IE and ΔN values of *n*-POX.

Based on the discussion above, it can be concluded that the 3-POX molecules have many active centers of negative charge. In addition, the areas containing N and O atoms are the most possible sites of bonding metal surface by donating electrons to the metal iron. According to these results, we could calculate the quantum chemical parameters before the experiment to forecast the inhibitor effectiveness. This can help improve accuracy and save time.

At present, more and more researchers are engaged in the calculation of the quantum chemistry of the organic heterocyclic inhibitors, especially the nitrogen-heterocyclic inhibitors. El Sayed et al. [23] proceed the quantum chemical calculation for corrosion inhibitions of some triazole, oxadiazole, and thiadiazole derivatives by using a Restricted Hartree-Fock (RHF) method. Arslan et al. [24] took the quantum chemical studies on the corrosion inhibition of

some sulphonamides by using density functional theory (DFT) and some semiempirical methods. Their useful results validated the accuracy of our calculations and results from their other analytic angles.

5. Conclusions

The relationships between inhibition efficiency of iron in perchloric acid solution and E_{HOMO} , $E_{\text{HOMO}} - E_{\text{LUMO}}$, and ΔN of *n*-POXs were calculated by DFT method. The inhibition efficiency increased with the increase in E_{HOMO} and decrease in $E_{\text{HOMO}} - E_{\text{LUMO}}$. 3-POX had the highest inhibition efficiency because it had the highest HOMO energy and ΔN values, and it was most capable of offering electrons. The distribution of electronic density shows that the molecules of *n*-POXs had many negatively charged active centers. The electron density was found to be positively correlated with nitrogen and oxygen atoms, which resulted in increasing inhibition efficiency. The areas containing N and O atoms are most possible sites for bonding the metal iron surface by donating electrons to the metal.

Quantum chemical calculations indicated that considering only one parameter is not convenient; hence several parameters or a composite index of more than two or more quantum chemical parameters were taken into consideration to characterize the inhibition activity of the molecules. Quantum chemical calculation approach is adequately sufficient to also forecast the inhibitor effectiveness using the theoretical approach. Moreover, it may be used to find the optimal group of parameters that might predict the structure and molecule suitability to be an inhibitor.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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