

Review

Performance of Organic Molecules as Corrosion Inhibitors for CS: A Comprehensive Review

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Abstract- Organic molecules have occupied an important place by researchers and chemists in the field of corrosion inhibition of metals in various corrosive media such as HCl. Owing to the property of adsorption on the metal surface by the interaction of heteroatoms (O, N, P, S), rings, and double bonds exist in the molecules with the vacant orbital on a metallic surface. These interactions lead to the adsorption of molecules on the metal surface, forming an inhibitory layer, thus decreasing the corrosion rate of the metal, and increasing the inhibition efficiency. The review begins with a history of corrosion inhibitor molecules, then the effect of structure, substitution, heteroatoms, and chain length existing in the molecules on the inhibition efficiency. Comparative study of the inhibitory performance of corrosion inhibiting molecules using weight loss (WL), electrochemical impedance spectroscopy (EIS) techniques, and Potentiodynamic polarization (PDP). Adsorption isotherm models and global quantum chemical descriptors (GQCD) were applied to understand the relation between inhibition efficiency and molecular structure. This summary investigates and evaluates specific organic molecules and their inhibition efficiency in corrosive environments.

Keywords- Organic molecules; Corrosion inhibition; Steel; Efficiency inhibition; WL/EIS/PDP analysis; GQCD

1. INTRODUCTION

Corrosion is the most interesting phenomenon to study, the destruction of metal in the face of a corrosive solution such as hydrochloric acid, sulfuric acid, nitric acid and phosphoric acid used for cleaning in the industry, such as iron pickling, chemical cleaning, descaling boilers, and acidification of oil wells in oil exploration [1]. Corrosion of metals and alloys is a problem of concern that significantly affects both the economy and safety [2]. To avoid this metal loss, several compounds as inhibitors are used. The use of organic compounds as corrosion inhibitors are beneficial due to heteroatoms such as sulfur, nitrogen, phosphorus, oxygen, and benzoic rings, also double bonds, and chain length [3]. In general, these compounds prove to be very effective corrosion inhibitors. The capacity of organic compound due to the adsorption onto a metal surface and replace the water molecule determines its efficacy as an inhibitor [4]. The effectiveness of these compounds depends on the electron density around the heteroatom, the number of adsorption sites in the molecule and their charge density, the size of the molecule, the adsorption mode, and the formation of metal complexes on the surface [5].

Recently, previous researchers have studied and investigated the anticorrosion behavior of Carbon Steel in a corrosive medium using organic molecules, to evaluate their effect on corrosion inhibition efficiency. These molecules are rich in heteroatoms, benzoic rings, and double bonds that facilitate attachment to the metal surface. Ecofriendly heterocyclic compounds, biomolecules extracted from nature, and ionic liquids have been considered protective coatings due to their environmental and health impacts. The present review gathers specific works in the field of corrosion inhibitors in Hydrochloric acid. In addition, we have provided the results obtained from each molecule. Thus, a detailed description of the existing types of organic corrosion inhibitors.

2. ORGANIC MOLECULES AS CORROSION INHIBITORS

2.1. Corrosion inhibitor

Corrosion inhibitor defined by the NACE «An inhibitor is a chemical substance which, when added in small concentrations to an environment, effectively checks, decreases, or prevents their action of the metal with the environment ». However, this definition avoids considering as inhibitor additives that, while meeting the second condition (reduction of the rate of corrosion), do not meet the first (for example, the adjustment of pH by adding a base or an acid is not a means of inhibition in the sense of the definition). Conversely, certain compounds, which should be excluded in all rigor by the definition, can nevertheless be considered as inhibitors (oxygen-consuming additives: scavengers). Finally, the meaning given by this definition to the term inhibitor prevents corrosion inhibition from being interpreted in an overly semantic sense as the slowing down, by whatever means, of the corrosion process of a metal (for example, the incorporation of an alloying element into a metal: chromium is not an iron inhibitor when it is used in the composition of stainless steel).

2.2. Properties of molecules corrosion inhibitor

a) Adsorption

Organic compound as corrosion inhibitor typically works through surface adsorption. These compounds tend to adsorb below the optimal inhibitor dosage in a flat orientation. On the contrary, Inhibitors tend to adsorb vertically above the optimal concentration. As a result, below an ideal inhibitor dose, the metal/inhibitor attraction takes precedence, however, once optimal adsorption is reached, intramolecular inhibitor repulsion takes over. This behavior is affected by the type of organic inhibitor, the composition of metal, and the working circumstances (temperature, acid concentration, etc.) [6].

b) Length of the chain

Hydrocarbon chains of various lengths can be found in organic inhibitor compounds. The length of the alkyl chains attached to the inhibitor structure can significantly influence the hydrophobicity of the corrosion inhibitor [7]. Chain length, number of alkyl chains, free doubles in heteroatoms, and double bonds significantly influence the adsorption strength. Although long alkyl chains, increase hydrophobicity, they also affect bulkiness, which can pose inhibitor adsorption problems [8].

c) Structure and substitution

The nature, amount, and location of the heteroatoms, the type of the phenyl rings, and the functional groups connected to the corrosion inhibitor molecules may all have a role in the inhibitor's adsorption on the metal surface [9]. Corrosion inhibitors are usually organic molecules with 5 or 6 membered heterocyclic and phenyl rings [10]. Also, can contain different ring sizes, the increasing of the number of bonds double, heteroatoms and ring size lead organic molecules to have larger active adsorption sites with a higher surface coverage. Corrosion inhibitors may contain bonded substituent groups in their structure. By electro-attraction or electro-donation, these substituent groups higher or lower the electron density in the rings to which they are attached. The electro-donation substitute can be increases the electron density of the ring and vice versa with the electron attracting groups. Thus, the existence of electron-donating groups leads to a reduction in the efficiency of inhibition. On the other hand, electron donor groups improve efficiency [11].

In terms of molecular size, solubility, and electrical effects, substituents in molecules can have a variety of consequences of corrosion inhibition behavior. Substituents can cause a variation in the structure and size of molecular inhibitors, resulting in a variation in surface coverage and thus the effectiveness of protection. The addition of a polar substituent could improve the molecular solubility of the molecule in a corrosive medium, while a non-polar substituent lowers the solubility [12].

The most functional substituent cited as electron-donating types we found; methyl, primary and secondary amine, ether and halogens. The electron density was increasing within aromatic ring.

Contrarily, the functional groups such as nitrile, nitro, carbonyl compounds and acid are electron-attracting due to the decreasing of the anticorrosive behavior [10].

3. CLASSIFICATION OF CORROSION MOLECULES

3.1. Azoles

Azoles are heterocyclic compounds with an N atom and at least one additional non-carbon atom (S, O, etc.). They're aromatic and have two bonds double, which give rise to azolines and azolidines after sequential reduction. They're placed in a ring with five members. Furthermore, they are thought to be efficient corrosion inhibitors for the metal in a range of harsh situations. It has been shown that the nitrogen and sulfur atoms of the azole rings form coordinated connections with the metal oxide surfaces. They are particularly highlighted as the most effective copper corrosion inhibitors [6].

a)Pyrazole

Pyrazoles are heterocyclic compounds with two neighboring N atoms in C_3N_2 rings. Pyrazoles are mostly used in pharmaceuticals, due to the adsorption behavior through the single pair electrons of nitrogen (N) and the mobile electrons occurring in the ring of pyrazole, also inhibits metal corrosion [13]. To have a better interaction at the metal/inhibitor interface, it is better to use pyrazole derivatives with a higher electron density [14]. Zarrok et al. Studied the effect of corrosion inhibition of pyrazole derivatives of 2-[Bis-(3,5-dimethyl-pyrazol-1-ylmethyl)-amino]-3-hydroxybutyric acid' (Bip 2) for CS in 1 M HCl (Figure 1) and found the excellent inhibitory efficiency reach a maximum of 95.9, 93.8 and 92.9% at 10^{-3} M at 308K for WL, PDP and EIS, respectively [15]. Others have devoted their study to the theoretical behavior of bipyrazole derivatives, namely 5,5'-dimethyl-1'H-1,3'-bipyrazole 4-carboxylate (Bip1) and 3-(bromomethyl)-5,5'-dimethyl-1'H -1,3'-bipyrazole (Bip3). They have been reportedly employed as CS corrosion inhibitors in 1 M HCl medium, the parameters were calculated to understand the molecular with the highest inhibition power, and according to the results obtained molecule Bip 3 is more effective than Bip1 [16].

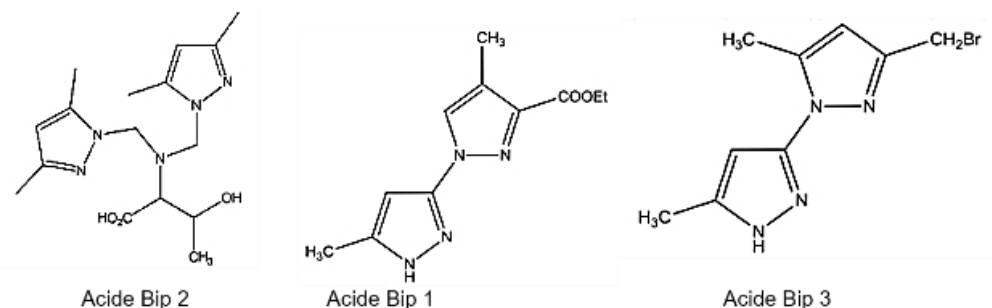


Figure 1. Molecular structure of Bip2, Bip1, and Bip3

b) Imidazole

Imidazoles are organic molecules with a chemical structure $C_3H_4N_2$, contain two nitrogen atoms in the five-membered heterocyclic rings at positions 1 and 3. They are important and consist of several biologically and industrially useful heterocyclic compounds. Due to these properties of water miscibility, highly polar nature, nucleophilic behavior, these compounds interact strongly with the metal surface, Therefore, it acts as an effective corrosion inhibitor for aqueous electrolytes. [17]. Several works applying imidazoles as anti-corrosion protection in corrosive media, including the effect of the molecule '4,5- Diphenyl-1H-Imidazole-2-Thiol' (DIT) with a concentration of 10^{-2} M on the anticorrosion behavior of CS35 in 1M HCl [18]. This molecule is effective in the acidic medium with inhibition efficiencies equal to 91.23, 92.74 and 89.75% for WL, PDP and EIS, respectively. Other research, in the framework of green chemistry, is used ionic liquids corrosion inhibition molecules of CS in acidic medium. The use of the molecules 1-hexyl-3-(4-phenoxybutyl)-1H-imidazol-3-iumbromide (MS35) and '3-(4-ethoxy-4-oxobutyl)-1-hexyl-1H- imidazol-3-iumbromide (MS36) with a concentration of 10^{-2} M and 308K, are tested and found that the molecule MS35 is the most effective, with inhibition efficiencies equal to 97.3% for MS35 compared to MS36 (93.7%) [19]. Figure 2 represents the structure of the molecules discussed above.

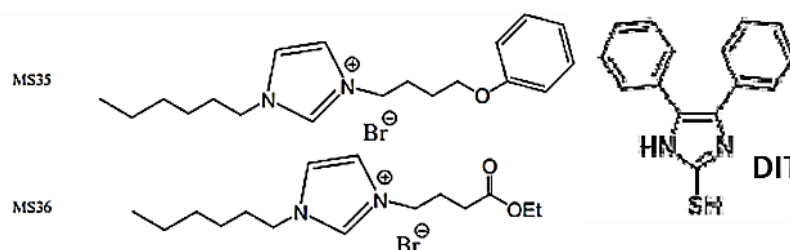


Figure 2. The chemical structure of the studied molecule DIT and ionic liquids MS35, MS36

3.2. Azine

Azine is a compound with a benzene structure when one of the C-H atoms is substituted with an N atom. Diazines are heterocyclic with two C-H substituted by two N atoms ($C_4H_4N_2$). The diazines are 1,2-, 1,3-, and 1,4-diazine, named Pyridazine, Pyrimidine, and Pyrazine. Also, Triazines have three C-H groups substituted by N atoms with the general formula $C_3H_3N_3$, namely 1,2,3-, 1,2,4- and 1,3,5-triazines [6].

a) Pyridine

Pyridazine is a 6 membered heterocyclic molecule having 2 N atoms nearby. The production of three aromatic diazines, Pyridazine, Pyrimidine, and Pyrazine, is caused by the substitution of the C-H unit in the pyridine ring. The existence of an N atom related to pyridine improves pyridine's properties and chemical characteristics of pyridine. The effect of Pyridazine on corrosion inhibition of metallic materials has been investigated in several studies, the structure of molecules used is shown in Figure 3. The use of 6-phenylpyridazin-3(2H)-one (GP0) with a concentration of 10^{-2} M

as an inhibitor for mild steel in corrosive media, resulted in inhibition coefficients of 82.7 and 80.4% for PDP and EIS, respectively [20]. Another study focusing on the effect of inhibition of 2-(3-methyl-6-oxopyridazin-1(6H)-yl)aceto-hydrazide (GK1) with a concentration of 10^{-3} M on the corrosion of mild steel in HCl, the inhibition efficiency obtained are 74.2, 73.4 and 74.5% for WL, PDP and EIS, respectively [1].

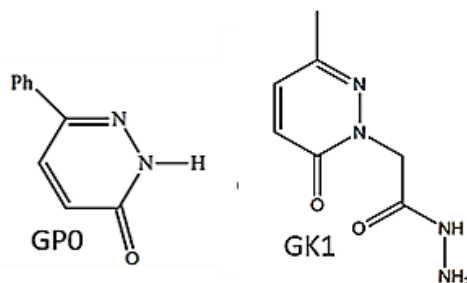


Figure 3. Molecular structure of **GP0**, and **GK1**

3.3. Quinoline

Quinoline is a chemical compound that has a pyridine molecule fused to a benzene ring, with a bicyclic nitrogen heterocyclic structure having a molecular formula of C_9H_7N . Properties of quinoline include solubility in hot water and organic solvents [21]. According to statistics, the annual production of quinoline is over four tons. These compounds have unlimited applications in industrial and biological fields [22].

a) Quinoxaline

Benzopyrazine or Quinoxaline is a compound with a combined benzene and pyrazine ring structure. Quinoxaline isomers are Quinazoline, Cinnoline, and Phthalazine [23]. They are molecules of synthetic origin in the laboratory and rarely in nature. The application of quinoxalines is generally in herbicides, dyes, fungicides, and antibiotics [24]. Also, due to the tendency to protonate in acidic media, which facilitates adsorption onto metal substrates, quinoxaline is used in the inhibition of metal corrosion [25]. Figure 4 shows the derivatives of quinoxaline, namely 1-[4-acetyl-2-(4-chlorophenyl) quinoxalin-1(4H)-yl] acetone (Q2), has been studied as a corrosion inhibitor of steel in aggressive 1M HCl medium, at temperature range from 308 to 343K. The inhibition coefficients obtained with a concentration of 10^{-3} M is 95.8% by Weight Loss at 308K. This efficiency decreases with increasing temperature to 73.2% at 343K [26]. Another derivative, 2-(4-(2-ethoxy-2-oxoethyl)-2-p-tolylquinoxalin-1(4H)-yl) acetate (Q3), under the same conditions, was studying the effects of temperature on the corrosion of CS in 1 M HCl medium with and without various concentrations of Q3.

The inhibition coefficients obtained at 10^{-3} M concentration is 97.4% by Weight loss at temperature 308K, decreasing with increasing temperature to 31.3% at 343K [27].

Another study, the anticorrosion behavior of CS in aerated 1 M HCl medium with 10^{-3} M of 3,7-dimethylquinoxaline-2-(1H)-one (DQO) at 308K was evaluated. The inhibition efficiency was 98% PDP and 96.8% EIS [2].



Figure 4. Structure of quinoxaline corrosion inhibitors Q2, Q3, and DQO

3.4. Amine

Theoretical corrosion inhibition is studied based on the theoretical functional density parameters of the two molecules 4-methylbenzene-1, 2-diamine (AMPA), and Benzene-1, 2-diamine (BD), their chemical structure is represented in Figure 5. They have reported that the AMPA molecule is better in corrosion inhibition than BD [28]. The same researchers studied the corrosion inhibition effect of the AMPA molecule using WL, PDP, and EIS with a concentration of 10^{-3} M, the inhibition coefficients for each analysis are 66.9%, 66.6%, and 66.7% respectively at 303 K [29].

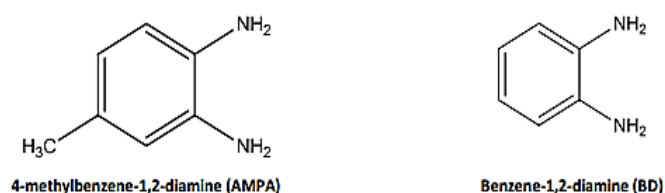


Figure 5. Chemical structure of molecules AMPA and BD

3.5. Pyrane

A Pyrane ring is a six-membered heterocyclic ring with two double bonds, five carbon atoms, and one oxygen atom. The basic chemical structure is C_5H_6O . There are two isomers of Pyrane that differ in the carbon-carbon double bond position. In 2H-pyran, the double bonds are in the 2 and 4 positions, whereas in 4H-pyran they are in the 2 and 5 positions. A study was carried out to evaluate the effect of a derivative of Pyrane molecules, the effect of 'ethyl 6-amino-5-cyano-2-methyl-4-(p-tolyl)-4H-pyran-3-carboxylate' (Pyr2) shown in Figure 6 on the corrosion of mild steel in 1.0 M HCl was investigated using a concentration of 10^{-3} M, the coefficients obtained are 76.6% PDP, and 75% EIS, at 298K [30].

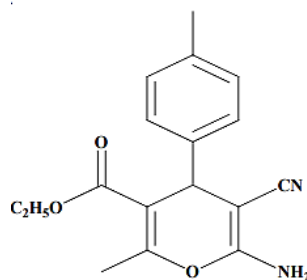


Figure 6. Structure of molecule **Pyr2**

3.6. Biomolecules

Recently, several researchers have been investigating the inhibition of steel corrosion using biomolecules extracted from plants and algae. For example, the inhibition efficiencies of Anemone Coronaria Extract (ACE) on the corrosion behavior of CS in 1M HCl were evaluated by [31], for a concentration of 2g/L obtaining inhibition coefficients of 94.6% WL, 90.1% PDP, and 92% EIS at 298K. The inhibitory action of Oxycedrus Juniper Extract (JOE) against corrosion of CS in 1.0 M HCl solution was studied by [32], with a concentration of 6 g/L, the results of the coefficients 87% WL, 90.9% PDP, and 89.3% EIS at 298K.

4. MOLECULES AS CORROSION INHIBITORS

4.1. Weight loss

Gravimetric analysis or Weight loss is a better reflection of the corrosion phenomenon as it is in the real state. This method is easier to use and does not require a large amount of equipment, but does not allow for an approach to the mechanisms involved in corrosion. It allows the average corrosion rate to be assessed directly. The principal concept of WL is the measurement of the weight loss Δm of a surface sample S , during the time t of immersion in a corrosive solution maintained at a constant temperature [18].

The corrosion rate is given by the following equation:

$$W_{\text{corr}} = \frac{(m_i - m_f)}{S \times t}$$

where m_i , m_f , t and S are the initial mass, the final mass, the immersion time in hours and the surface area (cm^2), respectively.

The inhibitory efficiency of an organic compound requires the use of the following equation:

$$\text{IE}_{\text{WL}} (\%) = \frac{(W_{\text{corr}}^0 - W_{\text{corr}})}{W_{\text{corr}}^0} \times 100$$

W_{corr}^0 and W_{corr} are represent the corrosion rate values of the steel after immersion without and with inhibitor, respectively.

The significance of the results obtained by the weight technique:

➤ The elevation in the concentration of the molecules diminishes the corrosion rate. Furthermore, the increase in the inhibition efficiency indicates the corrosion inhibition behavior of the molecule [31].

➤ The increase of inhibitor concentration increases the corrosion inhibition efficiency, this indicates the adsorption of the molecule to form an adherent layer on the metal surface and suggests that covering the metal surface with this layer decreases the thickness of the double layer [18].

➤ Elevating the temperature decrease the corrosion inhibition efficiency, which suggests desorption of the adsorbed molecules from the metal surface [27].

All the molecules studied are classified according to their Corrosive medium, metal type, and corrosion inhibition coefficient. The representation was based on the inhibition coefficient in the following diagrams.

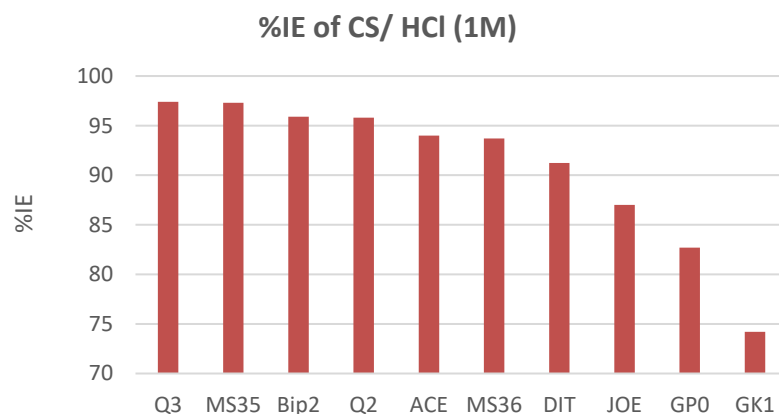


Figure 7. Graph represents the IE of all molecules studied in HCl (1M)

The molecules shown in the Figure 7 are used as anticorrosion compound of CS in acid medium (1M HCl). It is observed that the molecules 2-(4-(2-ethoxy-2-oxoethyl)-2-p-tolylquinoxalin-1(4H)-yl)acetate (Q3), 1-hexyl-3-(4-phenoxybutyl)-1H-imidazol-3-iumbromide (MS35), 2-[Bis-(3,5-dimethyl-pyrazol-1-ylmethyl)-amino]-3-hydroxybutyric acid' (Bip2), 1-[4-acetyl-2-(4-chlorophenyl)quinoxalin-1(4H)-yl]acetone (Q2), (ACE), '3-(4-ethoxy-4-oxobutyl)-1-hexyl-1H-imidazol-3-iumbromide' (MS36), '4,5- Diphenyl-1H-Imidazole-2-Thiol' (DIT) have perfect inhibition behavior with inhibition efficiencies equal to 97.3, 95.9, 95.8, 94, 93.7 and 91.23%, respectively. The molecules Q2 and Q3 were studied in a range of temperature from 308 to 343K, with a concentration of 10^{-3} M, the inhibition efficiency obtained is 95.8% for WL at 308K, this efficiency decreases to 73.2% (WL) at 343K, and 97.4% WL at temperature 308K, decreases to 31.3% at 343K, respectively. These results represent that corrosion inhibition of the molecules decreases with the increase of temperature, indicating desorption of these molecules with elevated temperature. On the other hand, the molecules 6-phenylpyridazin-3(2H)-one (GP0), 2-(3-methyl-6-oxopyridazin-1(6H)-yl) acetohydrazide (GK1), JOE have inhibition efficiencies are 82.7, 74.2 and 87%, respectively.

4.2. Electrochemical Analysis

a) PDP Analysis

Potentiodynamic polarization is a very good and useful technique to study the mechanisms of corrosion. Polarization curves [33] make it simple to understand the kinetics of anodic and cathodic processes. Readings are obtained with a given scan frequency and within a specific potential range [34].

The kinetics of corrosion processes can be measured using polarization methods. Electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic Tafel slope (β_c), anodic Tafel slope (β_a), and percentage inhibition efficiency (IE percent) as a function of inhibitor concentration are calculated using the polarization technique.

$$IE_{\text{PDP}} (\%) = \frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0} \times 100$$

Where i_{corr}^0 and i_{corr} are the corrosion density current without and with inhibitor, respectively [35].

➤ Variation of E_{corr} ; If the value of $E_{\text{corr}} > 85\text{mv}$ is compared to the blank solution, the inhibitor can behave as an anodic or cathodic type. If the E_{corr} value $< 85\text{mv}$, it will behave as a mixed type of inhibitor. The inhibitor successfully delays anodic as well as cathodic reactions and can therefore exhibit a mixed control type.

➤ The decrease in current density i_{corr} indicates excellent protection of the metal due to the formation of a thin layer [36].

The researchers used various molecules as corrosion inhibitors for CS in corrosive media, including hydrochloric acid. These molecules were investigated and studied by Potentiodynamic polarization, on the one hand, to determine their mode of inhibition action on the metal surface, and on the other hand to calculate their inhibition efficiency. The following Table 1, represents the abbreviation of the molecules with their mode of action under the experimental conditions, they are classified according to the inhibition efficiency of each molecule. All the molecules DQO, Bip2, DIT, JOE, GP0, Pyr2, GK1, and ACE are used as anticorrosion inhibitors in the HCl acid media.

The polarization curves obtained for all the molecules studied with different concentrations are presented in figure 8. Firstly, the molecule (DQO) acts as a mixed type corrosion inhibitor with an inhibition coefficient of 98%, while the molecules (Bip2) (DIT) (JOE) have the same types of Mixed inhibition but inhibition coefficients that exceed 90%. These molecules are considered as perfect corrosion inhibitors, thanks to their values of the inhibition coefficients, due to their mixed mode of action on the metal surface, also their structure that contains heteroatoms (O, N, S), and the 5 and 6 chain-rings, and to the values of the inhibition coefficients. In addition, the molecules (GP0) (Pyr2) (GK1) have the same modes of action and inhibition coefficients of 80.4%, 76.6%, and 73.4% respectively. On the contrary, the molecule (ACE) has a cathodic mode of action and an inhibition efficiency of 90.1%.

b) EIS Analysis

Electrochemical Impedance Spectroscopy (EIS) is a proven and powerful tool for studying corrosion. Surface properties, electrode kinetics, and mechanical information can be obtained from impedance plots. [37]. This technique is necessary to obtain additional information on the corrosion inhibition of a particular compound. EIS measures the resistance and capacitance of a material by applying an excitation signal. Impedance spectroscopy is used to determine the charge transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}) and using these parameters, the inhibition efficiency is calculated according to the equation below [38], the capacitive loop in the EIS plots can be related to the charge transfer reaction and the electrical double layer formed on the metal surface [39]. If the adsorption of the inhibitor is correct, there is an increase in the value of R_{ct} and a decrease in the value of C_{dl} by increasing the inhibitor concentration.

$$IE_{EIS} (\%) = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100$$

Where R_{ct}^0 and R_{ct} are the charge transfer resistance in the absence and the present of inhibitor, respectively.

The parameters and their significance in the Nyquist curves are listed below:

- The diameter of the semicircle in the Nyquist plots increases with increasing corrosion inhibitor concentration, resulting in increased charge transfer resistance R_{ct} , revealing that the corrosion rate decreases as well as increasing inhibition efficiency [40].
- An increase in the R_{ct} value indicates the adsorption of molecules and the formation of a layer on the metal surface. This layer acts as a protective barrier and serves to decrease the charge transfer reaction on the metal surface, thus increasing the inhibition efficiency.
- A decrease in the value of the double-layer capacitance and increase in R_{ct} is attributed to a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer on the surface of the metal [30].

Table 1. Abbreviations, type of inhibition action, nature of the metal and medium and inhibition efficiency of the molecules evaluated as corrosion inhibitors using PDP and EIS measurements

Inhibitors	Concentration/ Metal/ Medium/T	Type of inhibition	PDP (%)	EIS (%)
(DQO)	10 ⁻³ M / CS / HCl (1M) / 308K	Mixed Inhibitor	98	96.8
(Bip 2)	10 ⁻³ M / CS / HCl (1M) / 308K	Mixed Inhibitor	93.8	92.9
(DIT)	10 ⁻² M / CS / HCl (1M) / 298K	Mixed Inhibitor	92.78	89.75
(JOE)	6 g/l / CS / HCl (1M) / 298K	Mixed Inhibitor	90.9	89,03
(ACE)	2 g/l/ CS / HCl (1M) / 298K	Cathodic inhibitor	90.1	92
(GP0)	10 ⁻³ M / CS / HCl (1M) / 308K	Mixed Inhibitor	80.4	80.4
(Pyr2)	10 ⁻³ M / CS / HCl (1M) / 298K	Mixed Inhibitor	76.6	75
(GK1)	10 ⁻³ M / CS / HCl (1M) / 308K	Mixed Inhibitor	73.4	74.5

The study of the anticorrosion behavior of Carbon steel in a corrosive solution of hydrochloric acid, using molecules as corrosion inhibitors. These studies were investigated by researchers using a very important tool to explain what happens at the molecule/metal interface, namely electrochemical impedance spectroscopy. The molecules used as corrosion inhibitors, the conditions under which they were studied, and the inhibition efficiency of each molecule is presented in Table 1.

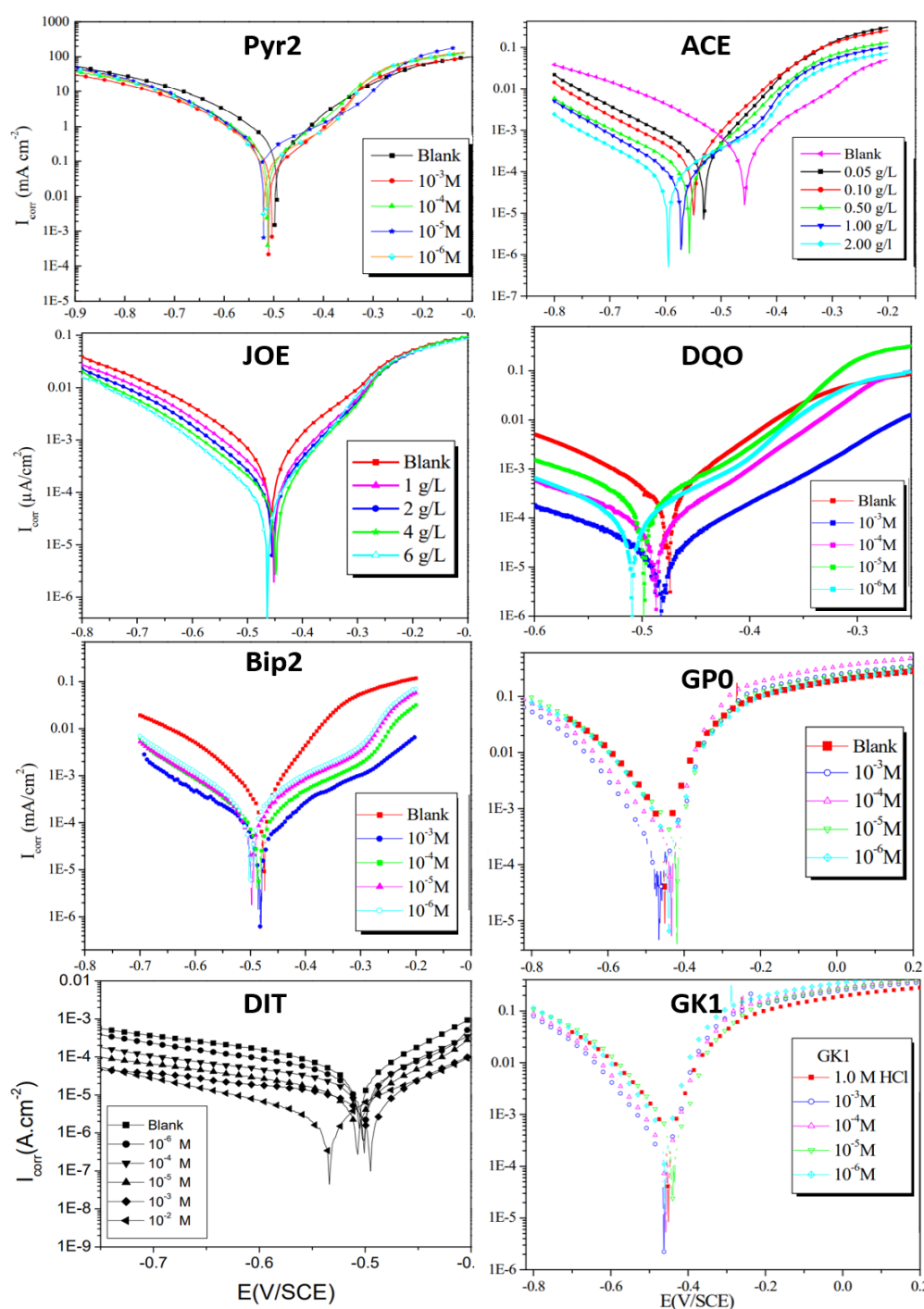


Figure 8. Polarization curves of molecules investigated as corrosion inhibitors in HCl medium (1M)

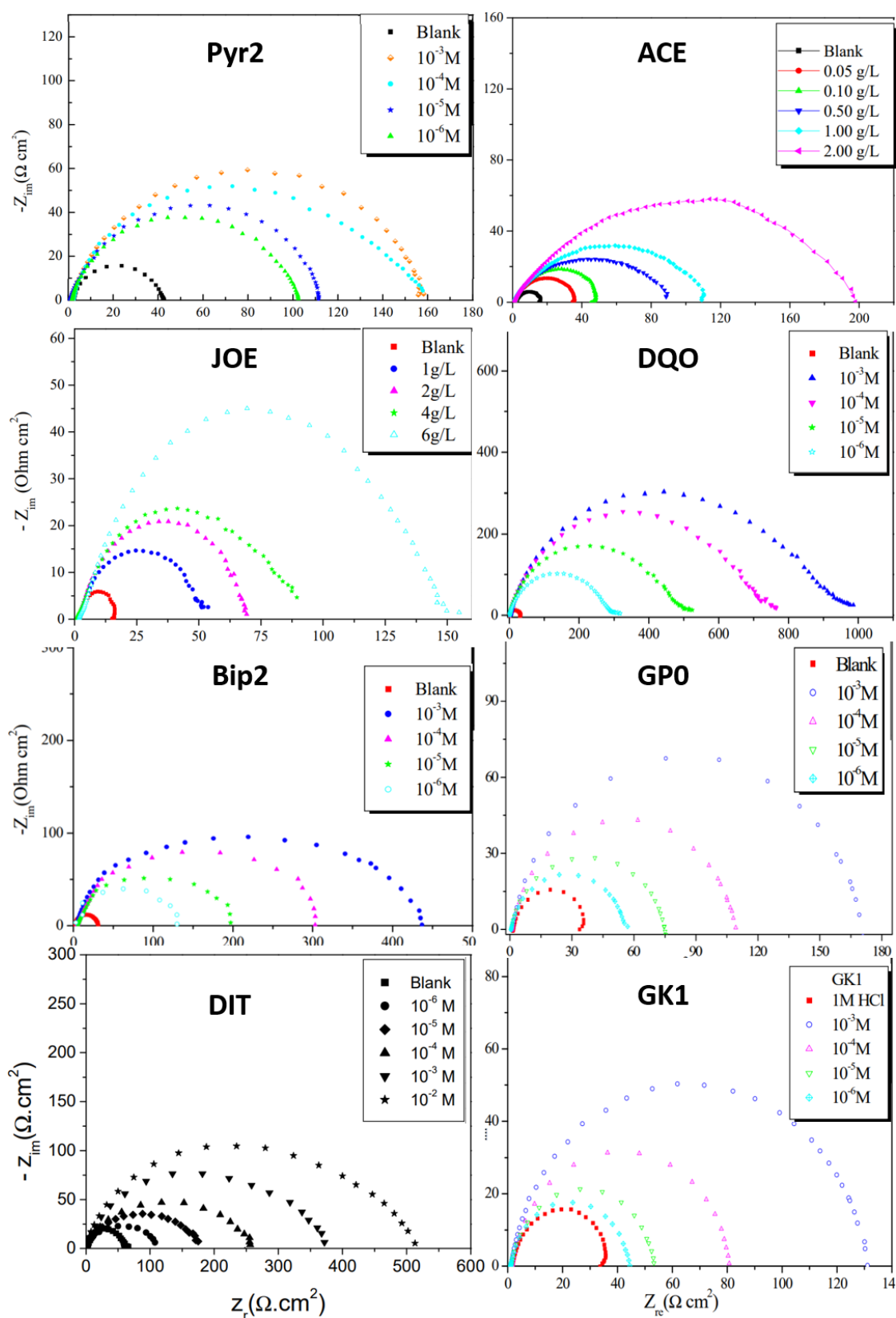


Figure 9. Nyquist plots of molecules investigated as corrosion inhibitors in HCl medium (1M)

The inhibition efficiency of these molecules was calculated using the charge transfer resistance according to the equation mentioned above. Table 1 shows the abbreviations, the nature of the metal and electrolytes and the inhibition efficiency of the molecules evaluated as corrosion inhibitors in

HCl media using EIS measurement. From these results, we can say that the molecules DQO, Bip2, and ACE have a good inhibition efficiency of 96.8%, 92.9%, and 92% respectively. While the molecules DIT, JOE, GP0, Pyr2, and GK1 have inhibition coefficients of 89.75%, 89.03%, 80.4%, 75%, and 74.5% respectively.

From the results obtained using the Nyquist plot presented in Figure 9, all of the compounds Pyr2, ACE, JOE, DQO, Bip2, JP0, DIT, and GK1 are used as a CS corrosion inhibitor in HCl 1M. The change in loops form with the elevation of corrosion molecule concentration, indicates an increase in charge transfer resistance. An increase in charge transfer resistance with increasing concentration of inhibitor indicates an increase in the electrical double layer on the metal surface, suggesting that the inhibitor acts by adsorption on the metal surface [32]. An increase in R_{ct} and a decrease in the value of the double-layer capacitance C_{dl} is attributed to a decrease in the local dielectric constant and an increase in the thickness of the electrical double layer on the surface of the metal. The adsorption of molecules in the surface of the metal is made through the existence of Cycles that are rich in electrons, in addition to the heteroatoms that have free doublets, allows a better interaction of the inhibitor towards the metal surface, which indicates the formation of a protective layer on the surface, thus decreasing the rate of corrosion and subsequently increasing the inhibition efficiency.

4.3. Adsorption Analysis

Adsorption models and thermodynamic parameters are basic information to understand the interaction inhibitors/metal interface, using adsorption isotherms. To determine the mechanism of organo-electrochemical reactions.

Table 2. Represents the types of adsorption isotherms, models, and their curves

Adsorption Isotherm	Models	Curves
Freundlich	$\text{Log } \theta = \text{Log } K + \frac{1}{n} \log C$	$\text{Log } \theta$ vs $\log C$
Langmuir	$\frac{C}{\theta} = \frac{1}{K_{ads}} K_{ads} + C$	$(\theta / 1 - \theta)$ vs $\log C$
Temkin	$K_{ads} \cdot C = e^{\theta}$	θ vs $\log C$
Frumkin	$K \cdot C = \frac{\theta}{1 - \theta} e^{\frac{\theta}{1 - \theta}}$	θ vs $\log C$

The organic compound can be adsorbed on the metal surface by a substitute adsorption process with water molecules already adsorbed on the metal surface [19]. Surface coverage values with and without inhibitor concentrations, obtained from weight loss measurements were used to explain the best isotherm and to determine the type of adsorption process [41]. The values of surface coverage for different doses of inhibitor in HCl 1 M media were analyzed using the most often used models: Freundlich, Langmuir, Temkin, and Frumkin, which are depicted in Table 2 [42].

The effectiveness of the inhibitor depends on the type and number of active sites on the metal surface, the charge density, the molecular size of the inhibitor, the interaction of the metal with the inhibitor, and the formation of the metal complex, among the parameters that are evaluated to know the adsorption behavior of the molecules on the surface of the metal mentioning:

- The high value of the adsorption constant K_{ads} reflects the increasing adsorption capacity of molecules on the metal surface [26].
- The relatively high and negative adsorption free energy ΔG_{ads}° may indicate relatively strong and spontaneous adsorption of molecules on carbon steel, which explains its high corrosion inhibition efficiency [26].
- Negative ΔG_{ads}° standard free energy values below 20 kJ / mol are associated with electrostatic interactions (physical adsorption) between charges molecules and charged metal surfaces. A negative value of 40 kJ / mol or more means that a coordinate covalent bond is formed by charge sharing or transfer of inhibitor molecules to the metal surface (chemisorption) [41].

Studies of the adsorption behavior of the molecules (DQO, Q2, Q3, Bip2, Pyr2, DIT, GK1, GP0, MS35, and MS36) corrosion inhibitor at the inhibitor/metal interface in HCl medium. Table3, represents the molecules, the parameters to which are studied, the free enthalpy ΔG_{ads}° , the adsorption finding K_{ads} , and the mode of inhibitor/metal interaction.

Table 3. Abbreviations, Nature of metal and Electrolytes, ΔG_{ads}° and K_{ads} of molecules evaluated as corrosion inhibitors

Molecule	Concentration /metal/ solution/ T	ΔG_{ads}° (Kj/mol)	K_{ads} (M ⁻¹)	Interaction Inhibitor/metal
DQO	10 ⁻³ M / CS / HCl (1M) / 308K	- 47.47	2029830.39	Chemisorption
Q2	10 ⁻³ M / CS / HCl (1M) / 308K	- 44.20	565511.70	Chemisorption
Q3	10 ⁻³ M / CS / HCl (1M) / 308K	- 40	110391.835	Chemisorption
Bip 2	10 ⁻³ M / CS / HCl (1M) / 308K	- 40.92	507045.4	Chemisorption
Pyr2	10 ⁻³ M / CS / HCl (1M) / 298K	- 41.91	400036.8	Chemisorption
DIT	10 ⁻² M / CS / HCl (1M) / 298K	- 34	16536.66	Physico-chemisorption
GK1	10 ⁻³ M / CS / HCl (1M) / 308K	- 38.22	54796.62	Physico-chemisorption
GP0	10 ⁻³ M / CS / HCl (1M) / 308K	- 39.21	80596.4	Chemisorption
MS35	10 ⁻² M / CS / HCl (1M) / 308K	- 41.63	207120.8	Chemisorption
MS36	10 ⁻² M / CS / HCl (1M) / 308K	- 34.49	12752.8	Physico-chemisorption

The adsorption behavior differs from one molecule to another, all the studied molecules obeyed the Langmuir model. The molecules DQO, Q2, Q3, Bip2, Pyr2, GP0, and MS35 act on the metal surface with a chemisorption mode, i.e. the formation of a covalent bond between the molecule and the vacant orbital of the metal surface. Thanks to their tendency to share electrons

with the metal surface for the formation of this bond. While the molecules DIT, GK1, and MS36 have a mixed behavior since they react with a chemisorption and physisorption mode. We suppose that this difference in the mode of inhibitor/metal interaction could be due to the existence of heteroatoms, rings, double bonds resulting from interactions and sharing of their electrons with the vacant orbital of the metal surface. Thus, the better adsorption of molecules on the surface of CS leads to the formation of a protective layer. Furthermore, increasing inhibition efficiency and decreasing the corrosion rate.

4.4. Theoretical functional density

Quantum chemistry studies are useful methods to explain the effectiveness of inhibitor molecules against the corrosion of CS as well as the molecular or electronic structure of the inhibitor [26]. Theoretical functional density also provides a more detailed understanding of the mechanism of action of the inhibitor [43].

Table 4. Indication and formulas to calculate the parameters of the theoretical functional density

Parameter	Formulas of calculating	Indication
Highest Unoccupied Molecular Orbital	E_{HOMO} (eV)	A high E_{HOMO} value means that the inhibitor molecule can easily donate an electron. [26].
Lowest Unoccupied Molecular Orbital	E_{LUMO} (eV)	The lowest value of E_{LUMO} means that the metal will accept electrons [28].
ΔE_{gap} (eV)	$\Delta E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}$ (eV)	The energy gap (ΔE) between HOMO and LUMO reflects the stability of the molecule. The smaller ΔE , the easier it is for the molecule to polarize and adsorb to the metal surface [30].
Dipole moment	μ (Debye)	Higher dipole moment (μ) values support a strong inhibitor-sample interaction, whereas lower values indicate a buildup of inhibitor molecules surrounding the electrode surface [29].
Electronegativity	$\chi = -\frac{1}{2} (E_{\text{LUMO}} + E_{\text{HOMO}})$ (eV)	The lower values of hardness η and electronegativity χ imply the reactivity of the inhibitor and the tendency to be adsorbed at the sample [19].
Chemical hardness	$\eta = \frac{1}{2} (E_{\text{LUMO}} - E_{\text{HOMO}})$ (eV)	
Global softness	$\sigma = \frac{1}{\eta}$ (eV^{-1})	The high softness value also describes the responsiveness and the inhibitory capacity of the inhibitor [30].
Fraction transferred electrons	$\Delta N = \frac{\chi_{\text{Fe}} - \chi_{\text{inh}}}{2(\eta_{\text{Fe}} + \eta_{\text{inh}})}$	The value of ΔN showed the inhibitory effect due to electron donation. If $\Delta N < 3.6$ (electron), Suppression efficiency increases with the value of ΔN , while it decreases if $\Delta N > 3.6$ (electron) [31]. The higher ΔN increases the %IE and thus the better compound as an inhibitor [16].

The calculations allow us to determine the charge distribution of the molecules [44]. The molecular frontier orbital theory is used to gain insight into the interaction of inhibitors with metal

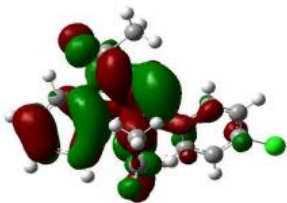
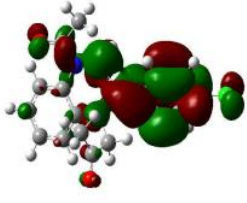
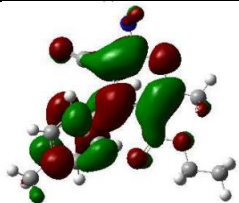
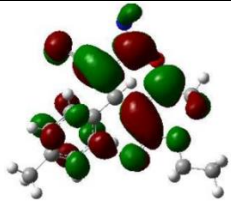
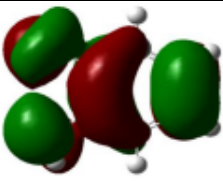
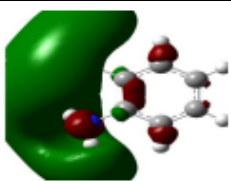
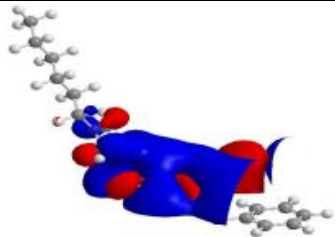
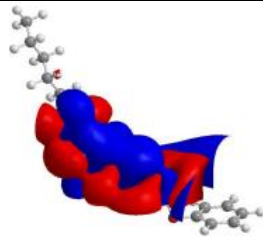
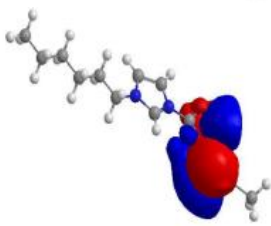
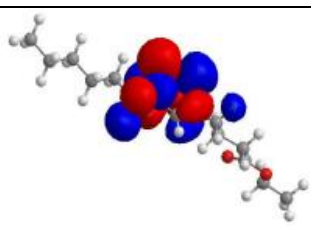
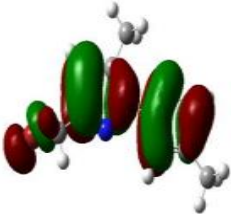
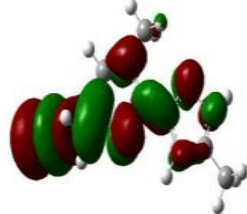
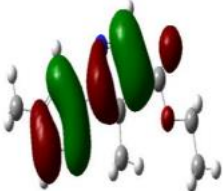
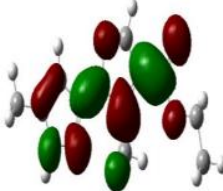
surfaces. According to this theory, chemical reactivity is calculated by the interaction of the inhibitor with the sample's highest orbital (HOMO) and lowest molecular orbital (LUMO) [45]. The HOMO energy (E_{HOMO}) represents the ability of the molecule to donate a lone electron pair. LUMO (E_{LUMO}) represents the ability of the molecule to accept electrons from a donor reagent. The ΔE_{gap} represents the difference between E_{HOMO} and E_{LUMO} [46]. To calculate chemical reactivity descriptors several formulas were used, such as the energy gap ΔE_{gap} , the dipole moment μ , the ionization potential I , the electron affinity (A), the electronegativity (X_{inh}), the chemical hardness (η), the global softness (σ) and the fraction of transferring electrons (ΔN). Table 4 represents the quantum parameters and the formulas for calculating each parameter, as well as their indication.

Table 5. Abbreviations, and DFT parameter of molecules studied as corrosion inhibitors

Molecules	Q2	Pyr2	BD	MS35	MS36	Bip1	Bip3
E_{HOMO} (eV)	-5.0645	-6.3130	-5.39753	-0.421	-0.437	- 6.1136	-5.9603
E_{LUMO} (eV)	-1.28607	-4.9797	-0.40083	-0.466	-0.423	- 0.5593	-0.5075
ΔE_{gap} (eV)	3.778	1.3333	4.99671	0.045	0.014	5.5543	5.4528
μ (debye)	2.6660	7.4032	1.21250	31.638	15.781	5.5500	5.3501
X (eV)	3.1752	5.64635	2.89918	0.4435	0.43	3.33645	3.23393
η (eV)	1.88921	0.66665	2.49835	-0.022	0.007	2.77715	2.72643
σ (eV ⁻¹)	0.52932	1.5000	0.40026	45.45	-----	0.36008	0.36678
ΔN	1.0122538	1.015263	0.316373	-149	-----	0.65958	0.69065
Behavior	Donor	Acceptor	Donor	Donor /acceptor		Donor	

Table 5, represents the molecules used as corrosion inhibitors of metal in hydrochloric acid (Q2, Pyr2, MS35, MS36, Bip1, and Bip3). The higher values of E_{HOMO} mean that the molecules Q2, Bip1, and Bip3 have an electron-donating behavior, indicating the better adsorption and formation of the layer at the metal surface. On the other side, the molecule Pyr2 has an electron acceptor behavior which is in agreement with the adsorption studies. While the molecules MS35, MS36 have a donor-acceptor behavior in agreement with their adsorption result by chemisorption, chemisorption/physisorption interaction respectively. The low values of energy gap ΔE_{gap} , electronegativity X , hardness η of inhibitor molecules MS35, MS36, Pyr2, and Q2 indicate the high stability and reactivity of these molecules [30-19]. Table 6, shows the distribution of HUMO and LUMO densities in the structure of the studied molecules.

Table 6. Distribution of HOMO and LUMO in molecular orbitals of the studied molecules

Molecules	HOMO	LUMO
Q2		
Pyr2		
BD		
MS35		
MS36		
Bip1		
Bip3		

For molecule 1-[4-acetyl-2-(4-chlorophenyl) quinoxalin-1(4H)-yl] acetone (Q2) The HOMO density of this molecule is distributed mainly in the quinoxaline ring which indicates

their ability to donate electrons. On the contrary, the LUMO density is localized on the Cl substituted ring of this molecule.

The ethyl molecule 6-amino-5-cyano-2-methyl-4-(p-tolyl)-4H-pyran-3-carboxylate (Pyr2) has a distribution of HOMO, and LUMO localized on the whole molecule. On the other hand, the molecules MS36, MS35 have a HOMO density distributed on the two oxygen of an ethoxy-4-oxobutyl group, and the phenoxybutyl group respectively, but the LUMO density is localized on the protonated imidazole group, and the protonated imidazole and phenoxybutyl group, respectively. For The Bip1 and Bip3 molecules, we can see that the density distribution of HOMO and LUMO electrons on the surface of each molecule is uniform, which is due to the density of its electron cloud π .

According to planned studies and other researchers, more negatively charged heteroatoms, the more likely they are to be adsorbed to the metal surface by a donor-acceptor reaction. Molecules that have a high dipole moment adsorb on the metal surface by interaction or by electron sharing between the inhibitor and the vacant orbital of the metal, which indicates a better formation of the protective layer on the metal surface [19-29].

5. CONCLUSION

The present work illustrates the effect and importance of using natural or synthetic molecules as corrosion inhibitors in different corrosive environments. The studies revealed that increasing the inhibitor concentration decreases the corrosion rate and vice versa for increasing the temperature. Thus, the corrosion of the metal is high without inhibitor and decreases in the presence of a very small amount of corrosion inhibitor molecules. The most effective methods to study the anticorrosion behavior are the Weight Loss (WL), to understand a first approach on the corrosion of the metal when it is put in contact with a corrosive medium, and several electrochemical techniques, notably the electrochemical impedance spectroscopy (EIS), the Potentiodynamic polarization (PDP), to discover the mode of action of the corrosion inhibitor molecules on the metal surface. Adsorption isotherms to evaluate the adsorption behavior of corrosion inhibitors on the metal surface which can be physical adsorption (physisorption) based on electrostatic interaction or chemical adsorption (chemisorption) which is the formation of a covalent bond between the inhibitor and the vacant orbital of the metal surface, depending on the adsorption strength. Density functional theory is based on quantum chemical analysis as an instrument to study the interaction between the surface of the metal and the inhibitor molecules. Also, the responsible substitution at a molecule of the inhibitor/metal interaction. The mechanism of attenuation of corrosion is not very clearly explained. Therefore, much work remains to be done to better understand the mechanism of corrosion inhibition. We need more rigorous experimental and theoretical explanations to better understand the corrosion inhibition of metals using different inhibitors.

Abbreviations

CS: Carbon-Steel

NACE: National Association of Corrosion Engineers.

pH: Hydrogen Potential

N, O, S: Nitrogen, Oxygen, Sulfide

WL: Weight loss

PDP: Potentiodynamiques Polarization

EIS: Electrochemical impedance spectroscopy

Bip 1: 5,5'-dimethyl-1'H-1,3'-bipyrazole 4-carboxylate

Bip2: '2-[Bis-(3,5-dimethyl-pyrazol-1-ylmethyl)-amino]-3-hydroxybutyric acid'

Bip3: 3-(bromomethyl)-5,5'-dimethyl-1'H -1,3'-bipyrazole

DIT: '4, 5- Diphenyl-1H-Imidazole-2-Thiol'

MS35: '1-hexyl-3-(4-phenoxybutyl)-1H-imidazol-3-iumbromide'

MS36: '3-(4-ethoxy-4-oxobutyl)-1-hexyl-1H- imidazol-3-iumbromide'

GP0: 6-phenylpyridazin-3(2H)-one

P2: 4-(2- chlorobenzyl)-6-hydrazino-3-methyl-1,6-dihydropyridazine

GK1: 2-(3-methyl-6-oxopyridazin-1(6H)-yl) acetohydrazide

Q2: 1-[4-acetyl-2-(4- chlorophenyl) quinoxalin-1(4H)-yl] acetone

Q3: 2-(4-(2-ethoxy-2-oxoethyl)-2-p-tolylquinoxalin-1(4H)-yl) acetate

BD: 4-methylbenzene-1, 2-diamine (AMPA), and Benzene-1, 2-diamine

Pyr2: 'ethyl 6-amino-5-cyano-2-methyl-4-(p-tolyl)-4H-pyran-3-carboxylate'

ACE: Anemone Coronaria Extract

JOE: Oxycedrus Juniper Extract

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