Nifedipine, a pyridine derivative, was investigated as a corrosion inhibitor for API 5L X-52 steel in 2 M HCl solution by potentiodynamic polarization, electrochemical impedance spectroscopy, and quantum chemical calculations. Statistical tools were used to compare results of the experimental methods. The results showed that nifedipine is capable of inhibiting the corrosion of API 5L X-52 steel in 2 M HCl solution. Potentiodynamic polarization results reveal that nifedipine functions as a mixed-type inhibitor and presents an inhibition efficiency of about 78% at 500 ppm. Impedance data reveal an increasing charge transfer resistance with increasing inhibitor concentration and also show comparable inhibition efficiency of about 89-94% at 500 ppm. Thermodynamic parameters imply that nifedipine is adsorbed on the steel surface by a physicochemical process and obeys Langmuir adsorption isotherm. The calculated molecular properties, namely the highest occupied molecular orbital energy, lowest unoccupied molecular orbital energy, chemical hardness, energy gap, dipole moment, electronegativity, and global nucleophilicity index, all show a positive relationship to the observed corrosion inhibition efficiency.

**Keywords:** Nifedipine, corrosion inhibition, electrochemical impedance, carbon steel, quantum chemical study

**1. Introduction**

The problem of metal corrosion in acid medium is a severe environmental setback in the field of oil and gas, fertilizer, metallurgical, and other manufacturing industries. The industrial cost involved in preventing the problems of corrosion is enormous and so there is a significant effort from industries to find inexpensive and efficient additives to control corrosion. Medicinal drugs are gradually emerging as promising candidates in their application as corrosion inhibitors chiefly due to their natural origin [1], non-toxicity [2] and eco-friendly attributes. The study utilizes a pharmaceutical drug, nifedipine, which has no established adverse toxicological and ecological effect on the environment [3-5]. A review [6] detailing most of the contributions made to literature on the use of pharmaceutical drugs as corrosion inhibitors reveals that their effectiveness depends on their chemical composition, molecular structure, and affinities for the metal surface. These substances contain reactive sites like oxygen, nitrogen, and/or sulphur atoms having lone pairs of electrons and aromatic rings with delocalized $\pi$ electrons that support their adsorption onto metal surfaces thus preventing corrosion. Furthermore, the author opines that the mechanism controlling the corrosion inhibition of drugs on various metal surfaces still requires sufficient research both experimentally and theoretically to substantiate any mechanism. Morad et al. [7] reported a study on cefatrexyl in the corrosion inhibition of iron in chloride, sulphate and phosphate media using polarization and electrochemical impedance spectroscopy methods. The author proposed that the formation of soluble Fe(II)-cefatrexyl-Cl complex was responsible for the low inhibition performance of cefatrexyl in chloride solution and claimed that the compound adsorbed through the outer surface of iron by the formation of adsorbed ion pairs. Eddy et al. [8,9] in their work on the inhibitory action of penicillin proposed that physical adsorption of the compound onto the mild steel surface was via weak intermolecular interactions and that the strength of interaction between penicillin and steel surface is always variable and dependent on adsorption active centers. The adsorption and inhibitive effect of ceftezole for the corrosion of mild steel in HCl solution was reported by Singh and Ebenso [10] employing weight loss, electrochemical impedance spectroscopy, and Tafel polarization techniques. The results showed an increase in inhibition efficiency with increase in inhibitor concentration and temperature. Potentiodynamic polarization results gave evidence of a mixed type inhibitor
of its function and Langmuir adsorption isotherm was obeyed. The significance of the present study is based on the premise that corrosion inhibition and protection of metals or alloys play important role in chemical industries of any economy. Therefore this paper seeks to evaluate the potential of nifedipine, a pharmaceutical drug, as a suitable alternative to highly expensive and toxic corrosion inhibitors, using experimental and quantum chemical approaches.

2. Experimental

2.1. Materials

The API 5L X-52 steel specimen was taken from a portion of a carbon steel pipeline with chemical composition in weight % as follows; C(0.22), Mn(1.40), Si(0.45), P(0.025), S(0.015), Cr(0.20), Ni(0.02), Ti(0.04), Nb(0.15), Mo(0.08), V(0.15), Al(0.030) and the balance Fe [11]. Nifedipine was obtained from Peace Land Pharmaceutical shop, Nديدم Usang Iso Road Calabar-Nigeria. All reagents were of analar grade. The steel samples were cut into dimensions of about (1×1×1) cm³, ground and polished using SiC paper up to #2000 grit size. These were mounted using epoxy resin with 1 cm² surface area exposed. Further preparation of the steel surface entailed polishing, cleaning with distilled water and acetone and drying in cool air.

2.2. Preparation of inhibitor stock solution and electrochemical measurements

The inhibitor solution was prepared as previously described [12]. A GAMRY Reference 600 potentiostat was used for the electrochemical measurements and controlled with Gamry Framework software. The analysis of the polarization and impedance curves was done using Echem Analyst software. A three-electrode electrolytic cell was utilized with a Pt plate and impedance curves was done using Echem Analyst software. Gamry Framework software. The analysis of the polarization for the electrochemical measurements and controlled with Gamry Framework software. A GAMRY Reference 600 potentiostat was used in cool air.

2.3. Theoretical approach

Simulations were done by Density Functional Theory (DFT) electronic program Dmol–1 using Material Studio 4.0 software, in combination with the B3LYP functional. DFT/ B3LYP is known to produce good estimates of molecular properties that are related to molecular reactivity [13]. The molecular properties that are obtained by DFT/ B3LYP include the energy of highest occupied molecular orbital (EHOMO), energy of the lowest unoccupied molecular orbital (ELUMO), ionization potential (IP), electron affinity (EA), electronegativity (χ), global hardness (η), global softness (σ) and dipole moment (μ). Obi-Egbedi et al., [14], defined these quantities based on Koopman’s theorem. The values of the total electronic energy gives the IP and EA of the inhibitor. The ionization potential Eq. (1) and electron affinity Eq. (2) are related to the EHOMO and ELUMO respectively. Energy gap ΔE, can be calculated as illustrated in Eq. (3).

$$IP = -EHOMO$$

$$EA = -ELUMO$$

$$\Delta E = ELUMO - EHOMO$$

The parameter, global hardness η Eq. (4) measures the resistance of the atom to transfer charge whereas global softness σ describes the capacity of an atom or group of atom to receive electrons. It is estimated as the reciprocal of global hardness (Eq. (5)) [13].

$$\eta = -\frac{1}{2}(EHOMO - ELUMO)$$

$$\sigma = \frac{1}{\eta}$$

The global electrophilicity index ω is always estimated by using the electronegativity and chemical hardness parameters as given in Eq. (6).

$$\omega = \frac{\chi^2}{2\eta}$$

A high value of electrophilicity describes a good electrophile while low electrophilicity value describes a good nucleophile. Electronegativity gives the power of an electron or group of atoms to attract electrons towards itself. According to Koopman’s theorem, electronegativity can be estimated using Eq. (7).

$$\chi = -\frac{1}{2}(EHOMO + ELUMO)$$

The fraction of electrons transferred δ is usually evaluated following Eq. (8);

$$\delta = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})}$$

where χFe and χinh are the electronegativity values of Fe and inhibitor respectively while ηFe and ηinh are the global hardness of Fe and inhibitor respectively. The values of χFe and ηFe are considered as 7 eVmol⁻¹ and 0 eVmol⁻¹ respectively [15]. From the simplest molecular orbital theory model, additional electrons would occupy the lowest unoccupied molecular orbital (LUMO) and ionization electrons would be removed from the highest occupied molecular orbital (HOMO).
3. Results and discussion

3.1. Potentiodynamic polarization curves

The potentiodynamic polarization curves for API 5L X-52 steel in 2 M HCl solution at 303 K in the absence and presence of different concentrations of the inhibitor are given in the Tafel plots of Fig. 1. Corrosion current densities $I_{corr}$, corrosion potentials $E_{corr}$, anodic and cathodic Tafel slopes ($\beta_a$ and $\beta_c$, respectively) were obtained from the Tafel plots using Echem Analyst software and are listed in Table 1. The surface coverage $\theta$ and inhibition efficiency $IE$ was calculated by applying Eq. (9) and Eq. (10);

$$\theta = \frac{I_{corr}(blank) - I_{corr}(inh)}{I_{corr}(blank)}$$

(9)

$$IE = \frac{I_{corr}(blank) - I_{corr}(inh)}{I_{corr}(blank)} \times 100$$

(10)

where $I_{corr}(blank)$ and $I_{corr}(inh)$ are the corrosion current densities in the absence and presence of inhibitor respectively.

![Potentiodynamic polarization curves for API 5L X-52 steel in 2 M HCl solution in the absence and presence of different concentrations of nifedipine at 303 K](image)

**Fig. 1.** Potentiodynamic polarization curves for API 5L X-52 steel in 2 M HCl solution in the absence and presence of different concentrations of nifedipine at 303 K.

<table>
<thead>
<tr>
<th>Inhibitor conc. (ppm)</th>
<th>$E_{corr}$ (mV)</th>
<th>$\beta_a$ (mV dec$^{-1}$)</th>
<th>$\beta_c$ (mV dec$^{-1}$)</th>
<th>$I_{corr}$ ($\mu$A cm$^{-2}$)</th>
<th>Surface coverage $\theta$</th>
<th>$IE$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>-446</td>
<td>102.3</td>
<td>454.2</td>
<td>560</td>
<td>0.3000</td>
<td>30.0</td>
</tr>
<tr>
<td>50</td>
<td>-445</td>
<td>112.7</td>
<td>95.6</td>
<td>392</td>
<td>0.3000</td>
<td>30.0</td>
</tr>
<tr>
<td>100</td>
<td>-430</td>
<td>92.8</td>
<td>119.9</td>
<td>361</td>
<td>0.3553</td>
<td>35.5</td>
</tr>
<tr>
<td>200</td>
<td>-445</td>
<td>74.3</td>
<td>117.2</td>
<td>291</td>
<td>0.4830</td>
<td>48.3</td>
</tr>
<tr>
<td>300</td>
<td>-439</td>
<td>83.0</td>
<td>156.1</td>
<td>248</td>
<td>0.5571</td>
<td>55.7</td>
</tr>
<tr>
<td>500</td>
<td>-440</td>
<td>78.2</td>
<td>83.7</td>
<td>125</td>
<td>0.7767</td>
<td>77.7</td>
</tr>
</tbody>
</table>

Only the cathodic slopes changed significantly compared to the reference sample indicating more inhibitory effect on cathodic sites. In addition it was observed that the anodic $\beta_a$ and cathodic $\beta_c$ slopes of the inhibitor solutions affect both reactions [16]. Generally, an inhibitor is said to be anodic or cathodic type if the displacement in the corrosion potential $E_{corr}$ of the inhibitor against the blank is greater than 85 mV while if the shift is less than 85 mV it can be regarded as mixed type [17]. In the present study, the inhibitor causes a minor change in $E_{corr}$ value with respect to the blank with a maximum displacement of 16 mV. The results suggests that the inhibitor acted as a mixed type inhibitor.

$I_{corr}$ values show a progressive decrease with increasing inhibitor concentration and a corresponding increase in inhibition efficiency. The result is reflective of the adsorption of inhibitor molecules at the steel surface [18].

3.2. Electrochemical impedance spectroscopy curves

Impedance measurements were carried out at 303 K after 30 minutes of immersion in 2 M HCl solution in the absence and presence of different concentrations of the inhibitor as shown in the Nyquist plots of Fig. 2. The capacitive loops are characterized by depressed semicircles and with increasing diameters as the concentration of the inhibitor increases. This shows that the inhibitor molecules provide increasing corrosion protection at the metal-solution interface. An equivalent circuit was proposed to fit the impedance spectra for the analysis of the impedance characteristics as shown in Fig. 3. The model considers a film resistance $R_f$ arising from the inhibitor molecule film adsorbed on the steel surface, a constant phase element (CPE) $Q_f$ associated with the adsorbed film, a charge-transfer resistance $R_{ct}$, a constant phase double layer $Q_{dl}$ and the solution resistance $R_s$. The impedance values obtained from the fit are presented in Table 2. Alternatively, the charge-transfer resistance could be obtained from the difference in impedance at low and high frequencies as suggested by Chami et al. [16] and denoted here as $R'_{ct}$. The double layer capacitance ($C_{dl}$) values were calculated from the frequency at which the imaginary of the impedance is maximal ($-Z_{max}$) using Eq. (11).

$$C_{dl} = \frac{1}{2\pi f_{max}R_{ct}}$$

(11)

The percentage inhibition efficiency based on charge-transfer resistance values was calculated using Eq. (12) and given in TABLE 2 as $IE$ and $IE'$ depending on the determination of the charge-transfer values.

$$IE = \frac{1}{1 - \frac{R_{ct}(blank)}{R_{ct}(inh)}} \times 100$$

(12)

where $R_{ct}(inh)$ and $R_{ct}(blank)$ are the charge transfer resistance with and without the addition of inhibitor respectively. The results in Table 2 reveal a general increase in $R_{ct}$ and $R'_{ct}$ values and decrease in $Q_{dl}$ and $C_{dl}$ values as the concentration of inhibitor increases. Both $IE$ and $IE'$ have comparable values and the
increase with increasing inhibitor concentration indicates that corrosion of API 5L X-52 steel in 2 M HCl solution is restricted by a charge-transfer process [16,19]. The decrease in $Q_{dl}$ and $C_{dl}$ values reflects an increase in the thickness of the electrical double layer as a result of the adsorption of the inhibitor molecules at the steel surface/solution interface. The film of adsorbed inhibitor molecules provides a barrier which prevents the corrosion process leading to an increased inhibition efficiency.

![Fig. 2. Nyquist plots of API 5L X-52 steel in 2 M HCl with different concentrations of nifedipine in 2 M HCl solution](image)

Fig. 2. Nyquist plots of API 5L X-52 steel in 2 M HCl with different concentrations of nifedipine in 2 M HCl solution

![Fig. 3. Equivalent circuit for the electrochemical process at the steel surface](image)

Fig. 3. Equivalent circuit for the electrochemical process at the steel surface

### 3.3. Adsorption isotherm

Adsorption isotherm is a model used in providing information on the interaction between the studied molecules and the metal surface. The degree of surface coverage for different concentrations of inhibitors was calculated for both measurement methods and tested on different adsorption isotherms. The experimental data fitted well using the modified Langmuir isotherm proposed by Villamil et al. [20] and given in Eq. (13);

$$\frac{C_{inh}}{\theta} = \frac{n}{K_{ads}} + nC_{inh}$$  

where $C_{inh}$ is the concentration of inhibitor, $K_{ads}$ is the equilibrium constant, $n$ the value of the slope in the Langmuir plot and $\theta$ as earlier defined. The plot of $C_{inh}/\theta$ versus $C_{inh}$ presented in Fig. 4 gives a straight line, signifying that the adsorption of molecules under consideration on the steel surface obeys Langmuir adsorption. The free energy of adsorption $\Delta G_{ads}$ (Eq. (14)) for the corrosion of API 5L X-52 steel in 2 M HCl in the presence of the inhibitor molecule is listed in TABLE 3, including the equilibrium constant and regression coefficient.

$$K_{ads} = \frac{1}{55.5} \exp \left( -\frac{\Delta G_{ads}}{RT} \right)$$

where 55.5 is the concentration of water in mol/L, $R$ is the universal gas constant in J mol$^{-1}$ k$^{-1}$, $T$ is the thermodynamic temperature in Kelvin.

![Fig. 4. Langmuir adsorption isotherm plots using Tafel and EIS results for the adsorption of nifedipine on steel in 2 M HCl](image)

Fig. 4. Langmuir adsorption isotherm plots using Tafel and EIS results for the adsorption of nifedipine on steel in 2 M HCl

**TABLE 2**

<table>
<thead>
<tr>
<th>Inhibitor conc. (ppm)</th>
<th>$R_s$ ($\Omega$ cm$^2$)</th>
<th>$R_f$ ($\Omega$ cm$^2$)</th>
<th>$Q_{dl}$ (S cm$^-2$)</th>
<th>$R_{ct}$ ($\Omega$ cm$^2$)</th>
<th>$Q_{dl}$ (S cm$^-2$)</th>
<th>$n_{dl}$</th>
<th>IE (%)</th>
<th>$R'_c$ ($\Omega$ cm$^2$)</th>
<th>$C_{dl}$ (mF cm$^-2$)</th>
<th>IE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank 0.2064</td>
<td>15.310</td>
<td>9.513×10$^{-3}$</td>
<td>0.8952</td>
<td>9.07</td>
<td>1.352×10$^{-4}$</td>
<td>0.3901</td>
<td>19.24</td>
<td>207</td>
<td>31.6</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.1768</td>
<td>11.430</td>
<td>6.940×10$^{-3}$</td>
<td>0.9070</td>
<td>19.89</td>
<td>5.660×10$^{-4}$</td>
<td>0.2547</td>
<td>54.4</td>
<td>142</td>
<td>58</td>
</tr>
<tr>
<td>100</td>
<td>0.1360</td>
<td>9.453</td>
<td>4.289×10$^{-3}$</td>
<td>0.9060</td>
<td>20.79</td>
<td>5.894×10$^{-4}$</td>
<td>0.3205</td>
<td>56.4</td>
<td>142</td>
<td>58</td>
</tr>
<tr>
<td>200</td>
<td>0.3288</td>
<td>8.745</td>
<td>8.876×10$^{-3}$</td>
<td>0.9780</td>
<td>36.75</td>
<td>3.757×10$^{-4}$</td>
<td>0.7712</td>
<td>75.3</td>
<td>142</td>
<td>58</td>
</tr>
<tr>
<td>300</td>
<td>0.3765</td>
<td>6.978</td>
<td>8.012×10$^{-3}$</td>
<td>0.9759</td>
<td>51.97</td>
<td>8.872×10$^{-4}$</td>
<td>0.8659</td>
<td>82.5</td>
<td>142</td>
<td>58</td>
</tr>
<tr>
<td>500</td>
<td>0.2860</td>
<td>2.693×10$^{-3}$</td>
<td>3.260×10$^{-3}$</td>
<td>0.9945</td>
<td>146.20</td>
<td>3.239×10$^{-4}$</td>
<td>0.7467</td>
<td>93.8</td>
<td>168.70</td>
<td>23</td>
</tr>
</tbody>
</table>
ecules is of a physical adsorption type. This type of adsorption is linked to electrostatic interaction between charged inhibitor molecules and the charged metal. However, values close to 40 kJ mol⁻¹ or higher entail a transfer of charges between the inhibitor and the metal surface reflecting chemisorption. The calculated \( \Delta G_{\text{ads}} \) value for the inhibitor molecule obtained from potentiodynamic polarization and electrochemical impedance spectroscopy data are 2.74 kJ mol⁻¹ and 2.77 kJ mol⁻¹ respectively, indicating that physisorption mode is likely to predominate.

3.4. Statistical consideration

To compare results obtained from the two experimental measurements we adopt a statistical tool such as the \( T_{\text{test}} \) statistical model. The model was used to compare results of the two methods at concentrations of 50 ppm, 200 ppm and 500 ppm. \( T_{\text{test}} \) experimental calculated value was obtained using Eq. (15);

\[
T_{\text{test}} = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{\frac{M N}{M + N}} S_p}
\]  

(15)

where \( M \) is the number of set of values in the first method and \( N \) is the number of set of values in the second method, \( \bar{x}_1 \) is the mean of result of the first method while \( \bar{x}_2 \) is the mean of result of the second method. The pooled standard deviation \( S_p \), was calculated using Eq. (16);

\[
S_p = \sqrt{\frac{\sum_{i=1}^{M} (x_i - \bar{x}_1)^2 + \sum_{j=1}^{N} (x_j - \bar{x}_2)^2}{M + N - 2}}
\]  

(16)

where \( x_i \) and \( x_j \) are the set of individual values for the first and second method respectively, \( M + N - 2 \) is the degree of freedom, \( df \). The \( T_{\text{test}} \) experimental and critical values are listed in Table 4. The results obtained indicate that \( T_{\text{test}} \) experimental value in the two methods was found to have lower \( T_{\text{test}} \) experimental value than the critical value at significant level \( \alpha = 0.005 \) and degrees of freedom, \( df = 4 \). This means that there is no significant difference between potentiodynamic polarization method and electrochemical impedance spectroscopy method, thus suggesting a good agreement in the results obtained from the two methods.

3.5. Chemical reactivity

The chemical structure of the inhibitor molecule is presented in Fig. 5. The IUPAC name is given as 5-dimethyl-2,6-dimethyl-4-(2-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxlate and molecular formula \( C_{17}H_{18}N_2O_6 \) with molecular mass of 346.34 g mol⁻¹. It is an antihypertensive drug and a derivative of pyridine. The optimized structure of the compound is shown in Fig. 6. Frontier molecular orbital diagrams have also been demonstrated in Fig. 7. Quantum chemical parameters were calculated using Eq. (1)-(8) and the results are presented in Table 5.
In the present study, the values of the total electronic energy gives the ionization potential and electron affinity of the compound, which are related to $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ values respectively. As mentioned earlier, these were generated from the computational simulations. From the molecular orbital theory model, additional electrons discharged in the gaseous atom in ground electronic state as illustrated in Eq. (17) signify ionization potential and is related to $E_{\text{HOMO}}$:

$$H_{(g)} \rightarrow H^+_{(g)} + e^- \quad (17)$$

Such electrons would occupy the LUMO as the electron affinity, Eq. (18):

$$Fe_{(g)} + e^- \rightarrow Fe^-_{(g)} \quad (18)$$

The $E_{\text{HOMO}}$ is often associated with electron donating ability of a molecule to the appropriate acceptor molecule with low energy and empty or partially filled molecular orbital. When the energy of the HOMO of a molecule is higher than the energy of the LUMO, it implies that such a molecule would have a greater tendency to facilitate adsorption and enhance inhibition efficiency [22-24]. The structural diagram of the HOMO shows a greater electron density than the LUMO, confirming electron donating ability of the molecule. Furthermore, the diagram reveals that the active centers of adsorption of the molecular specie on the surface of the steel is through nitrogen, oxygen and some carbon atoms. The importance of energy gap $\Delta E$ is also applied to predict the inhibition efficiency of a compound. $\Delta E$ is actually used to develop a theoretical model for explaining the structure and confirmation barrier in molecular systems. Therefore, the smaller the values of $\Delta E$ of a compound, the greater its inhibition efficiency. Our result for $\Delta E$ in TABLE 5 is within the recommended range of small energy gap as reported elsewhere [22,25,26]. Dipole moment is another indicator regularly used for the prediction of corrosion inhibition processes as it measures the polarity in a bond and the distribution of electrons in a molecule. Thus, molecules with high dipole moment form strong dipole-dipole interactions with metals resulting in strong adsorption onto the metal surface, leading to a greater inhibition efficiency [27]. The dipole moment obtained reveals a strong dipole-dipole interaction with the metal and is of similar range as values obtained by Elmsellem et al. [27] and Gao and Liang, [28]. A molecule with a large $\Delta E$ signifies a hard molecule and a small $\Delta E$ reflects a soft molecule. A soft molecule would easily offer electrons to an acceptor system than a hard molecule. Based on this principle, adsorption may occur at the point in a molecule where the absolute softness ($\sigma$) is high [22,27]. In other words, a molecule whose global hardness ($\eta$) is higher than global softness, illustrates the ability of a molecule to effectively inhibit the corrosion of steels. In line with the preceding argument and the results presented in Table 5, the inhibitor molecule shows tendency to suppress corrosion.

### 4. Conclusion

1. The molecule was found to inhibit the corrosion of API 5L X-52 steel in 2 M HCl solution. Inhibition efficiency increased with inhibitor concentration. Double layer capacitance decreased respect to the blank solution.
2. Polarization studies revealed that the inhibitor molecule functioned as a mixed-type inhibitor and the adsorption of the molecule on the steel surface obeys Langmuir isotherm model.

3. Statistical results showed that the two experimental methods employed are in good agreement with each other.

4. The study also describes the importance of quantum chemical method using Density Functional Theory in the design and selection of substances for the protection of metals in aqueous solution.

Acknowledgement

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