Investigating the Acidic Corrosion Inhibiting Properties of Dryopteris Hirtipes on Mild Steel in Acidic Solutions

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Abstract- ***The corrosion inhibition performance of ethanol extract of Dryopteris hirtipes (DH) on mild steel in 1 M HCl and 0.5 M H_2SO_4 solutions was studied using gravimetric and electrochemistry methods of corrosion monitoring. Computer simulation method was used to evaluate the relationship between the corrosion inhibition efficiency and the molecular structure of two active constituents of the inhibitor. The gravimetric results showed that corrosion inhibition efficacy increased steadily with concentration. Potentiodynamic polarization results revealed that the plant material functioned as a mixed type corrosion inhibitor for mild steel reducing both the anodic dissolution of metal and cathodic hydrogen ion reduction, electrochemical Impedance data and the computer simulation results confirmed that the corrosion reaction was retarded through the adsorption of the extract organic constituents on the mild steel surface.***

Indexed Terms- ***Corrosion, Simulation, Potentiodynamic Polarization, Dryopteris Hirtipes, Inhibition Efficiency***

I. INTRODUCTION

Steel and its alloys find applications in many industries in the areas of, automobile, petrochemicals, chemical metallurgical and many more (1-3) and these applications are attributed to special properties found in them which include electrical conductivity, mechanical strength, high thermal conductivities well as cost effectiveness (4-6). However, these special properties in mild steel fail to be displayed when in contact with aggressive environments such as acid and bases used in the industries due to the phenomenon of corrosion. Therefore, there is a need to look for materials that can effectively reduce corrosion reaction. The study of corrosion inhibition of metals using natural compounds has attracted considerable interest in the recent years (7-10). These materials function as corrosion inhibitors due to the availability of heteroatoms (nitrogen, oxygen and sulphur) which promote their adsorption on the surface of the metal thereby reducing the metal degradation in corrosive medium (11-15). Natural inhibitors are cheap, non-toxic and readily available (16-18).

Dryopteris hirtipes (DH) plays a major role in medicine due to its antioxidant, antibacterial, anti-inflammatory, and antitumor properties (19). This study investigates the corrosion inhibitive effects of the ethanol extract of *Dryopteris hirtipes* on mild steel corrosion in acidic solutions using both experimental and theoretical studies respectively. The reason for employing the computational study in this study is to unravel the correlation existing between the inhibitor efficiency and its electronic molecular structure. Furthermore, the work seeks to widen the application of *Dryopteris hirtipes* as an eco-friendly corrosion preventing additive for mild steel protection (20-22).

Figure 1 Image of *Dryopteris hirtipes*

II. MATERIALS AND METHODS

2.1 Material preparation

Mild steel specimen of composition (weight %) C - 0.30, Si – 0.30, Mn – 0.30, P – 0.045, S – 0.050, Cr – 0.064, Cu – 0.040, Ti – 0.04 (23) and the balance Fe

was applied in the corrosion experiments. The mild steel specimens were polished in wet environment using different grades (#150 – #1000) of silicon carbide abrasive paper, degreasing was achieved in acetone and the coupons were dried with warm air. Analytical grade reagents and chemicals were used in the preparation of solutions used for the experiments. The aggressive solution were prepared with HCl and H_2SO_4 and distilled water. The stock solution of the plant extract was prepared by dipping 25 g of the dried powder of the leaves of *Dryopteris hirtipes* in 1000 ml absolute ethanol for 72-h. the resultant solution was filtered with filter paper. The quantity of the plant material that was extracted into the stock solution was calculated by comparing the initial weight of the plant material with the weight of the dried residue. Test solution of concentrations 200 mg/L, 400 mg/L, 600 mg/L, 800 mg/L and 1000 mg/L were prepared from the stock solution by dilution.

2.2 Gravimetric method

Test coupons of dimension 3 x 3 x 0.14 cm (24) were used for the gravimetric experiments. These metals were abraded with silicon carbide abrasive paper, washed in distilled water, dried using acetone and air, weighed and kept in a desiccator for further use. The metals were subsequently suspended with hooks and rod in 300 ml beaker containing the working solution. The systems were left in an aerated and unstirred condition throughout the experiment. To determine the weight loss with respect to immersion time, the test specimens were retrieved in 24-h intervals, this was done continuously for 120 h, upon retrieval, the test specimens were dipped in a solution containing 20 % NaOH and 200 g/L zinc dust (25) to momentarily quench the corrosion reaction, thoroughly scrubbed using bristle brush, washed in distilled water, dried, re-weighed and returned to the test solution. The weight loss after each 24-h was determined by subtracting the weight at a particular time from the initial weight of the metal specimen.

2.3 Electrochemistry method

PAR-2273 Advanced electrochemical system workstation (26), fixed with a conventional three-electrode corrosion cell was used for all the electrochemistry experiments, the working electrode was the mild steel specimen while saturated calomel electrode and a platinum rode were used as the reference and counter electrodes respectively. The working electrode was encased in epoxy resin of exposed surface area of 1 cm^2. Aerated and unstirred conditions were maintained until 1800 s of immersion this enabled the stability of the OCP values. The reaction temperature was maintained at 30 ± 1℃. Electrochemical impedance spectroscopy experiments were conducted at corrosion potentials E_{cor} within the frequency range of 100kHz-0.1 Hz, the signal amplitude of perturbation was 5 mV. The potentiodynamic polarization experiments were performed under a potential range of $\pm 250\, mV$ versus corrosion potential, the scan rate was 0.333 mV/s (27),

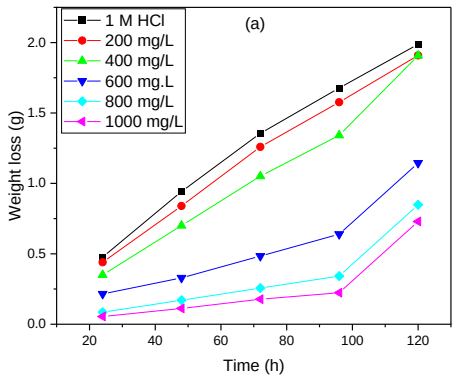
2.4 Theoretical simulation

All theoretical simulations were carried out in density functional theory (DFT) electronic structure programs DMol3 using the material studio 7.0 modelling software (28).

III. RESULTS

3.1 Gravimetric Results

To ascertain the effects of time and concentration on the corrosion of mild steel specimen in the absence and presence of the inhibitor in 1 M HCl and 0.5 M H_2SO_4, gravimetric experiments were conducted. Figure 2 illustrates the weight loss of mild steel in uninhibited and inhibited 1 M HCl (Figure 2a) and in 0.5 M H_2SO_4 (Figure 2b) as a function of exposure time. The results show that DH extract reduced the corrosion rates of mild steel in both acid environments. Figure 3 shows the trend of inhibition efficiency for various concentrations of the DH extract and as expected, efficiency increased steadily with DH concentration in both 1 M HCl and 0.5 M H_2SO_4 solutions.



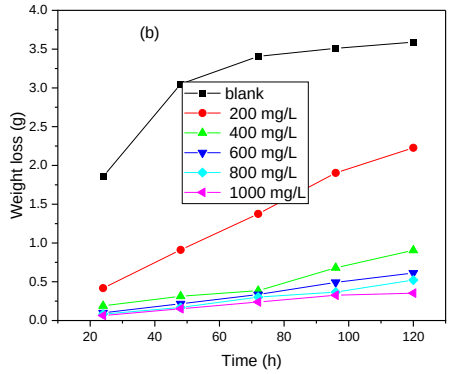
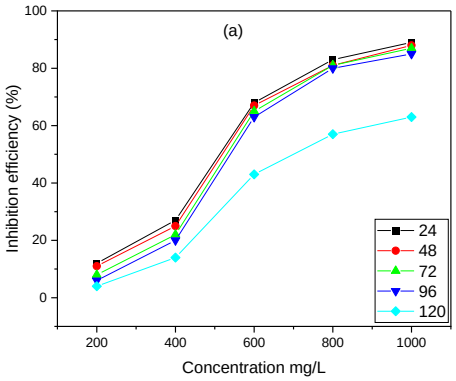


Figure 2 Weight loss vs time for mild steel corrosion in (a) 1 M HCl and (b) 0.5 M H_2SO_4 in the absence and presence of different concentrations of DH



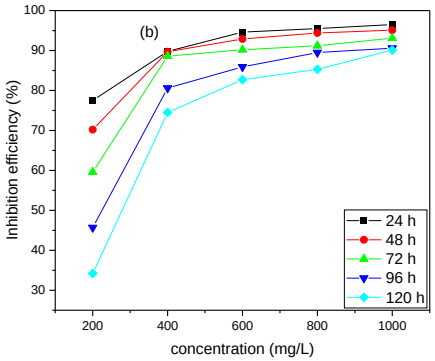


Figure 3. The inhibition efficiencies from the gravimetric data were estimated with the equation:

Inhibition efficiency was calculated from the gravimetric by the equation below:

$$IE(\%) = \left(1 - \frac{w_1}{w_2}\right) \times 100 \qquad (1)$$

Where w_1 and w_2 represent the weight loss of mild steel in the inhibited and uninhibited solutions respectively.

3.2 Electrochemistry Results

Electrochemistry experiments were undertaken to study the corrosion inhibition behaviour of DH from the electrochemistry point of view. The electrochemical impedance spectroscopy experiments were undertaken to gain insight into the kinetic of the electrochemical reaction. The impedance responses are presented in Figures 4 and 5 for mild steel corrosion in (a) 1 M HCl and (b) 0.5 M H_2SO_4 solutions in the absence and presence of various concentrations of DD extract in the Nyquist and Bode formats. In the two impedance graphs; the plot for the uninhibited sample was used as a reference. The Nyquist plots can be seen to have shown a depressed capacitive semicircle over the frequency range that was studied; this reveals a one-time constant in the Bode plots. The high-frequency intercept with the real axis in the Nyquist semicircles is allocated to the solution resistance (R_s) and the low-frequency intercept with the real axis is ascribed to the charge transfer resistance (R_{ct}). The obtained impedance data were fitted with an equivalent circuit models $[R_s(Q_{dl}R_{ct})]$(29-30), using ZSimpWin 3.10 software. In the equivalent circuit used, R_s is shorted by a

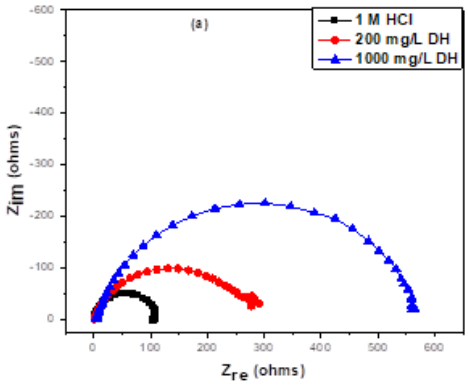
constant phase element (CPE) placed parallel with the R_{ct}. The use of CPE in place of a capacitor is to account for deviations from dielectric behavior that may arise from the inhomogeneous nature of the surface of the electrodes. The impedance of the constant phase element is given as below:

$$Z_{CPE} = Q^{-1}(j\omega)^{-n} \quad (2)$$

Where Q and n are the CPE constant and elements respectively. j is an imaginary number with value $j = (-1)^{1/2}$ while ω is the angular frequency in rad s^{-1} with value ($\omega = 2\pi f$) and f is the frequency in Hz. The impedance parameters estimated from the impedance data are presented in Table 1. The result revealed that the presence of the inhibitor increased the charge transfer resistance (R_{ct}) showing that the extract reduced the corrosion of mild steel in the acidic environments studied. The values of inhibition efficiency (IE%) were estimated from the electrochemistry impedance spectroscopy data as below:

$$IE\% = \left[\frac{R_{ct,inh} - R_{ct,bl}}{R_{ct,inh}}\right] \times 100 \quad (3)$$

$R_{ct,inh}$ is the value of the charge transfer resistance in the presence of the inhibitor whereas $R_{ct,bl}$ is the corresponding value in the absence of the inhibitor.



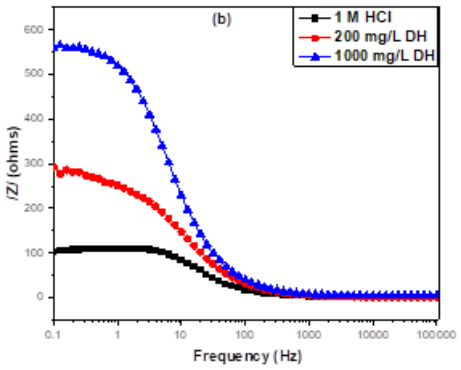
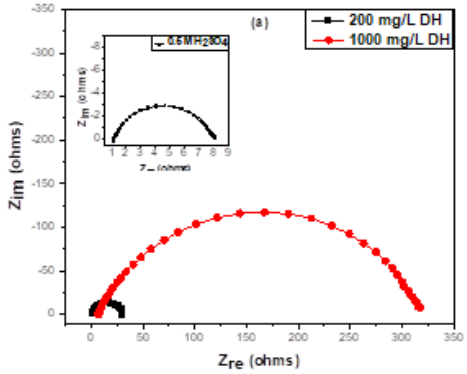


Figure 4. Electrochemical impedance spectra of mild steel in 1 M HCl solution without and with DH extract: (a) Nyquist and (b) Bode plot



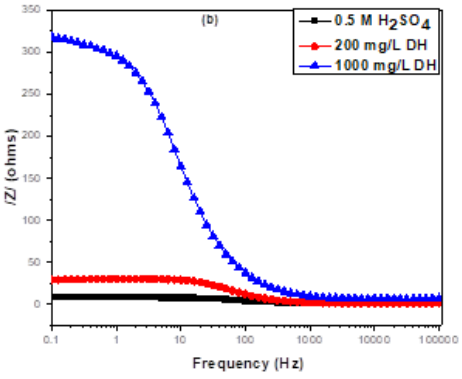


Figure 5. Electrochemical impedance spectra of mild steel in 0.5 M H_2SO_4solution without and with DH extract: (a) Nyquist and (b) Bode plots. Inset in panel (a) is the Nyquist plot in uninhibited acid.

Table 1. Electrochemical Impedance spectroscopy parameters for Mild Steel Corrosion in 1 M HCl and 0.5 M H_2SO_4 without and with DH Extract.

System	R_{ct} (Ω cm^2)	N	Q_{dl} ($\mu\Omega^{-1}S^n$ cm^{-2})	IE%
1 M HCl	104	0.88	91.7	
200 mg/L DH	264	0.87	22.4	60.6
1000 mg/L DH	554	0.88	24.2	81.2
0.5 M H_2SO_4	8.4	0.84	258.8	
200 mg/L DH	30	0.87	148.2	72
1000 mg/L DH	223	0.89	34.3	96.2

Potentiodynamic polarization (PDP) experiments were conducted to evaluate the effect of the DH inhibitor on the anodic and cathodic half reactions. Typical PDP plots for mild steel corrosion in the presence of different concentrations of DH at 303 K are presented in Figure 6 in (a) 1 M HCl and (b) 0.5 M 0.5 M H_2SO_4. The useful extrapolated electrochemical parameters for the reactions; corrosion potential(E_{corr}) and corrosion current densities (i_{corr}) acquired from the curves are listed in Table 2. The polarization plots showed that the addition of the extract effectively retarded both cathodic as well as the anodic half reactions bending the two half curves towards lower current densities at the same time shifting the corrosion potential (E_{corr}) slightly towards the more positive (anodic) position. The extract functioned as a mixed type corrosion inhibitor for mild steel in both acidic solutions. Inhibition efficiency was calculated from the polarization data by comparing the corrosion current density in with the extract $(i_{corr,inh})$ and the corrosion current density without the extract $(i_{corr,bl})$ as follows:

$$IE\ (\%) = \left(\frac{i_{corr,bl} - i_{corr,inh}}{i_{corr,bl}}\right) \times 100 \qquad (4)$$

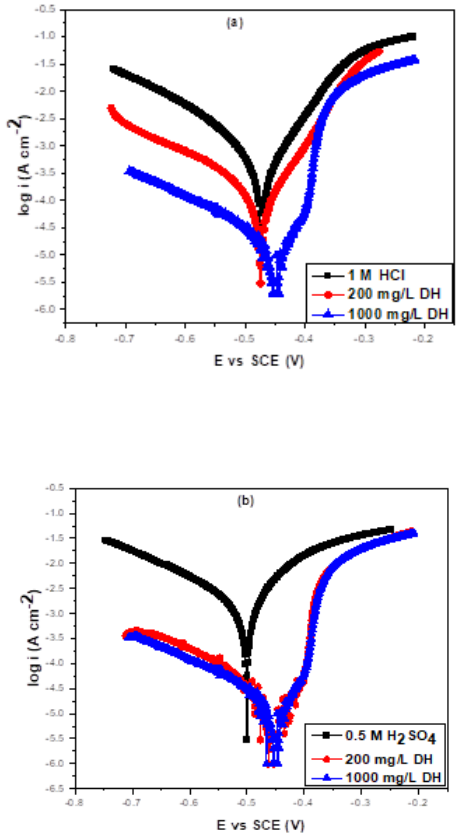


Figure 6. Potentiodynamic polarization curves of mild steel in (a) 1 M HCl and (b) 0.5 M H_2SO_4solution without and with DH extract.

Table 2. Potentiodynamic Polarization Polarization Parameters for Mild Steel in 1M HCl and 0.5 M H_2SO_4 in the Absence and Presence of DH extract

System	E_{corr} (mV vs SCE)	i_{corr} (µA/cm2)	IE%
1 M HCl	-471.3	649.4	
200 mg/L DH	-474.3	110.6	82.9
1000 mg/L DH	-448.9	14.1	97.8
0.5 M H_2SO_4	-500	2940	
200 mg/L DH	-491.4	357.5	87.8
1000 mg/L DH	-449	8.6	99.7

3.3 Theoretical Simulation Results

Corrosion inhibition reaction is a complex phenomenon involving many distinct processes

ranging from electron-cloud interactions to large scale processes such as self-assembly and associated with phase transitions. In recent time, there have been tremendous advancements in technology and with the available computational resources; it is possible to study such multiscale problems, as corrosion inhibition, using computational techniques. Various such studies are available. Chemical quantum calculations is a theoretical framework which gives better understanding of the existing relationship between molecular electronic structure and the corrosion inhibitive properties of the corrosion inhibitor. Density functional theory has proven to be a very important tool in quantum chemical computation as a result of its ability to simulate the geometry optimized molecular structure and predict the descriptors of chemical reactivity of an inhibitor (quantum chemical parameters) Hence, the performance of inhibitors based on their different molecular structures has been linked to their frontier molecular orbitals (highest occupied molecular orbital and lowest unoccupied molecular orbital). While the energy of the highest occupied molecular orbital (E_{HOMO}) measures the tendency of a specie to donate electron, the energy of the lowest unoccupied molecular orbital (E_{LUMO}) measures the tendency of the inhibitor to accept electron from a potential donor. High values of E_{HOMO} indicates better inhibition efficiency. The numerical value of the (E_{HOMO}) is directly related to the ionization energy ($I = -E_{HOMO}$) and the numerical value of the (E_{LUMO}) is related to electron affinity ($A = -E_{LUMO}$). The energy gap between the LUMO and HOMO energies (ΔE) is a function of reactivity of the inhibitor molecule towards its adsorption on the mild steel surface and $\Delta E = E_{LUMO-HOMO}$. The decrease in ΔE leads to increase in the reactivity of the molecule which increases the inhibition efficiency of the inhibitor. Two active chemical components of the DH (phytol [2-Hexadecen-1-ol, 3,7.11.15 tetramethyl] and 1-Hexadecene) extract were sourced from literature (31) and used for computational study. DFT computations were actualized using the electronic structure program DMol3 with a Mulliken population analysis (32). Electronic parameters for simulation include the Perdew−Wang (PW) local correlation density functionals and the restricted spin polarization using the DND basis set. Geometric optimization was achieved with COMPASS force field and Smart minimization methods. The quantum chemical parameters are presented in Table 3 while the Electronic properties are presented in Figure 7.for phytol and 8 for 1-Hexadecene The absolute electronegativity of the molecule (χ) and absolute hardness (η) were estimated using the equations below (33)

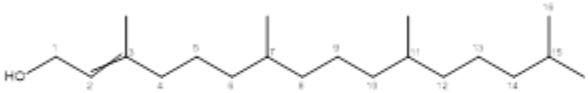
$$\chi = \frac{I+A}{2} \quad (5)$$

$$\eta = \frac{I-A}{2} \quad (6)$$

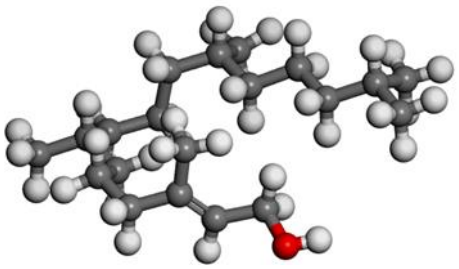
The charge transfered (ΔN) from the extract to the mild steel surface was calculated from the equation:

$$\Delta N = \frac{\chi_m - \chi_i}{2(\eta_m + \eta_i)} \quad (8)$$

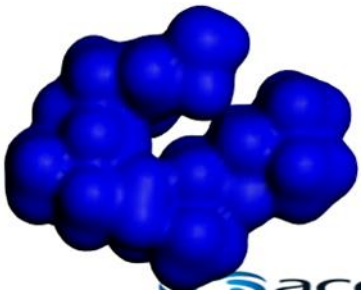
χ_m and χ_i represent the absolute electronegativity of the metal and inhibitor respectively whereas η_m and η_i represent the absolute hardness of the mild steel and the inhibitor. The values of ΔN shown in Table 3 were calculated using the theoretical values of 7 Ev/mol and 0 eV/mol for the χ_m and η_m respectively (34). Research has shown that ΔN correlate remarkably with adsorption energy for metal−inhibitor interactions, and larger values of ΔN corresponding to stronger adsorption. The values of the computational results presented in Table 3 show that the DH inhibitor functioned effectively for mild steel in the acidic media studied.



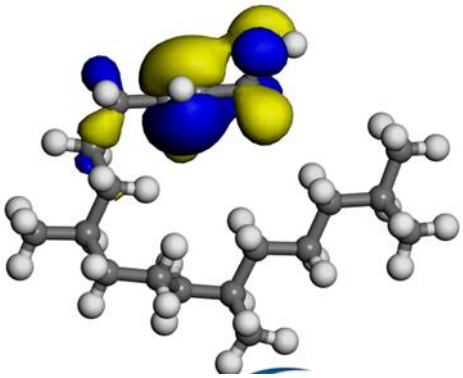
phytol



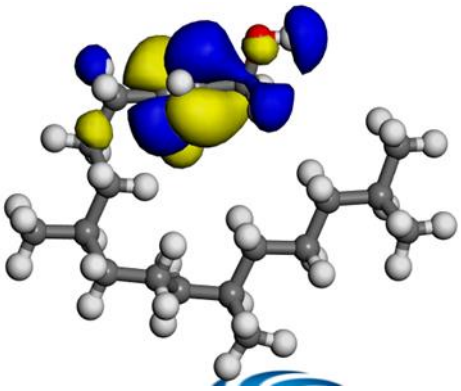
Optimized 3D structure



Electron density

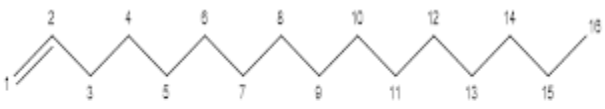


HOMO orbital

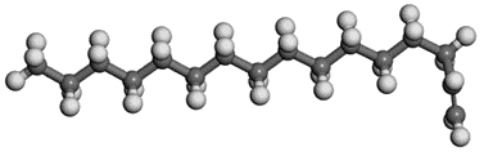


LUMO orbital

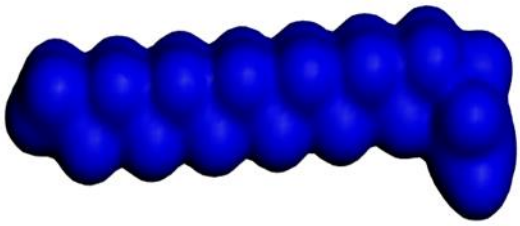
Figure 7 Electronic properties of phytol (2-Hexadecen-1-ol, 3,7.11.15 tetramethyl)



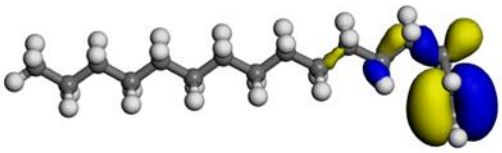
1-Hexadecene



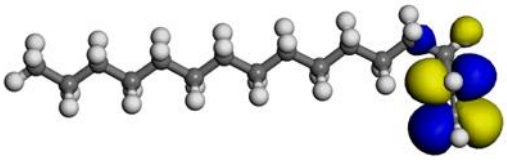
Optimized structure



Electron density



HOMO orbital



LUMO orbital

Figure 8. Electronic properties of 1-Hexadecene

Table 3. Calculated quantum chemical properties for the most stable conformations of Phytol (2-Hexadecen-1-ol, 3,7.11.15 tetramethyl) and 1-Hexadecene

Constituent	E_{HOMO} (	E_{LUMO}(eV	ΔE (eV)	χ	η	ΔN
Phytol	-0.2050	-0.0193	0.1857	0.1122	0.0929	37.0710
1-Hexadecene	-0.2213	- 0.014	0.2073	0.1177	0.1037	33.1837

CONCLUSION

The study showed that the ethanol extract of *Dryopteris hirtipes* retarded the acid induced corrosion of mild steel. The gravimetric results showed that inhibition performance increased steadily

with concentration. Potentiodynamic polarization results revealed that the inhibitor functioned as a mixed type corrosion inhibitor for mild steel, reducing the corrosion rate of the anodic and cathodic half reactions, electrochemical impedance spectroscopy and computational modeling results confirmed that the corrosion process was retarded by the adsorption of the extract constituents on the mild steel surface.

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