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Quantum Descriptors and Corrosion Inhibition Potentials of Amodaquine and Nivaquine

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Abstract

Amodaquine [4-[(7-chloroquinolin-4-yl) amino]-2-(diethylaminomethyl) phenol] and nivaquine (4-N-(7-chloroquinolin-4-yl)-1-N,1-N-diethylpentane-1,4-diamine sulphate) has been studied as potential source of green inhibitor for corrosion of aluminium in 1 M HCl at different concentrations using gravimetric method. To further elucidate the reactivity and efficiency of these anti-malaria drugs as potential corrosion inhibitors, quantum chemical calculations using Density Functional Theory (DFT) method in conjuction with Becke 3 Lee Yar Parr (B3LYP)/6-311++G** level of theory was applied. Kinetics and thermodynamic parameters central to surface adsorption were calculated and discussed. Results revealed that the inhibition efficiency increased as the inhibitor concentration increased but decrease with an increase in temperature with Nivaquine having better inhibition efficiency than Amodaquine. The adsorption of Amodaquine and Nivaquine on the surface of aluminium both followed the Freundlich adsorption isotherm at all concentrations and temperatures. The negative value of ΔG_{ads} obtained indicates spontaneous adsorption of the inhibitor on the aluminium surface and a low negativity indicates electrostatic interactions between inhibitor and the charged metal surface.

Keywords: Amodaquine; Nivaquine; Aluminium; Corrosion inhibition; DFT

Introduction

Corrosion, a constant and continuous problem, is the deterioration of metal by chemical attack or reaction with its environment. Although there are numerous options for controlling the corrosion of metals, the use of inhibitors is one of the best methods for protecting metals against corrosion. Severe corrosion problems arise due to the wide use of hydrochloric acid for pickling, descaling and cleaning processes of metal surfaces [1]. Aluminium show excellent corrosion resistance due to the formation of a thin and protective, naturally formed oxide film on its surface [2]. Unfortunately, when aluminium is exposed to aggressive environments such as acid pickling solutions, chemical etching, industrial cleaning or scale dissolving, these processes lead to significant mass loss of aluminium [3]. Corrosion inhibitor reported has involved the use of anti-malaria, sulpha, antifungal and antibacterial drugs, extracts from plants, because of the presence of hetero-atoms in the backbone of their structure as active centres, high solubility in water, high molecular size [4-6].

Theoretical chemistry has been used recently to explain the mechanism of corrosion inhibition, such as quantum chemical calculations. Recently, density functional theory (DFT) has emerged as a reliable and inexpensive method that is capable of successfully predicting the properties of the chemical systems [7]. It is important to create a synergy between experimental and computational studies to explain the adsorptive behaviour and mechanism of organic inhibitors. We have carried out previous work on the efficiency of Chloroquine as Corrosion Inhibitor for Aluminium [8]. Therefore, this article is devoted to study the inhibitory action of Amodaquine and Nivaquine for aluminium in hydrochloric acid using weight loss method and quantum chemical techniques.

Experimental Methods

Materials

The materials used for the study were aluminium sheets of composition (wt%): Si (0.125), Mn (0.0158), Cu (0.536), Zn (0.007), Ti (0.21), Fe (0.454), Sn (0.017), Pb (0.001) and Al (98.635) obtained from KOLORKOTE, Sango-Ota, Nigeria. Each sheet was mechanically pressed cut to form different coupons, each of dimension 4 cm by 3 cm by 0.45 mm. These coupons were used as supplied without further polishing, but were degreased in absolute ethanol, dried in acetone, weighed and stored in moisture free desiccators, prior to use. All reagents used for the study were Analar grade and distilled water was used for their preparation. Aggressive solution of 1 M HCl was prepared by dilution of analytical grade HCl (37.25%) with distilled water in a standard flask. Stock solution of Amodaquine and Nivaquine were each made in 50 ml ethanol and then made up to 1 dm³ of distilled water to have the highest concentration (10×10^{-3} M) from which other concentrations were prepared. The chemical structures of Amodaquine and Nivaquine are given in Figures 1 and 2.
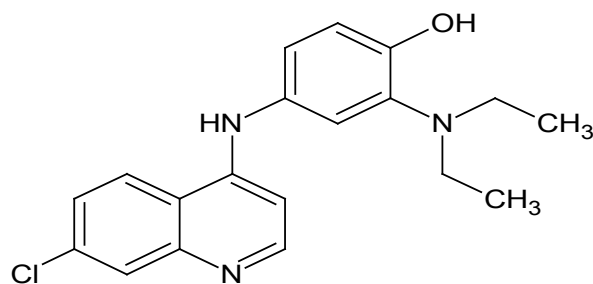
Gravimetric (weight loss) measurement

The gravimetric experiments were performed on a previously weighed aluminium coupon completely immersed in 50 ml of the test solution in an open beaker in absence and presence of different concentration of the inhibitors. The beaker was inserted into a water bath maintained at 30°C for 8 hours, the specimen were taken out, washed in a solution containing a mixture of 50% NaOH and 100 g/L of zinc dust. The washed coupons were dipped in acetone and allowed to air dry before re-weighing. The difference in weight was taken as total weight loss. The experiment was repeated at 60°C. From the evaluated

4-[(7-chloroquinolin-4-yl)amino]-2-(diethylamino)phenol

Figure 1: The chemical molecular structure of Amodaquine.
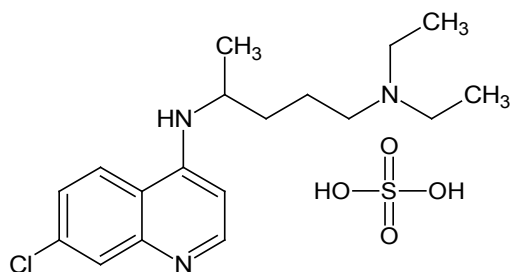
N^4-(7-chloroquinolin-4-yl)-N^1,N^1-diethylpentane-1,4-diamine sulphate

Figure 2: The chemical molecular structure of Nivaquine.

Temperature (°C)	Concentration (M)	Corrosion Rate (× 10⁻³mg/cm hr)	Inhibition efficiency (%)	Surface Coverage
	Blank	5.61	.	.
	2 × 10⁻³	3.75	33.07	0.3307
	4 × 10⁻³	3.3	41.14	0.4114
30°C	6 × 10⁻³	2.81	49.94	0.4994
	8 × 10⁻³	2.26	59.61	0.5961
	10 × 10⁻³	1.86	66.83	0.6683
	Blank	5.98	...	...
	2 × 10⁻³	4.23	29.37	0.2937
60°C	4 × 10⁻³	3.75	37.31	0.3731
	6 × 10⁻³	3.29	45.01	0.4501
	8 × 10⁻³	2.78	53.53	0.5353
	10 × 10⁻³	2.41	59.24	0.5924

Table 1: Calculated values of corrosion rate (CR), surface coverage (Θ) and Inhibition Efficiency (%IE) of aluminium corrosion in different concentration of Amodaquine at 30°C and 60°C.

weight loss, the inhibition efficiency (% IE) of the inhibitor, degree of surface coverage (Θ) and corrosion rates (CR) were calculated using equations (1)-(3) respectively [9,10].

$$\%IE = \frac{(W_2 - W_1) \times 100}{W_2} \qquad (1)$$

$$\theta = \frac{(W_2 - W_1)}{W_2} \qquad (2)$$

$$CR\left(mg / cm^2 / h\right) = \frac{W}{At} \qquad (3)$$

Where W_1 and W_2 are the weight losses (g) for aluminium in the presence and absence of the inhibitor in HCl solution; Θ is the surface coverage of the inhibitor; A is the area of the aluminium coupons (in cm²); t is the period of immersion (in hours) and W is the weight loss of aluminium after time, t. All the measurements were performed in triplicate and the mean value recorded.

Computational details

Quantum descriptor calculations were performed using Density Functional Theory (DFT), B3LYP with 6-311++G**. The quantum descriptors obtained were E_{HOMO}, E_{LUMO}, E_{LUMO}-E_{HOMO} (E_g), Total energy, Dipole moment (μ), The absolute electronegativity (χ), The absolute hardness (η), softness (σ) where obtained using Koopman's reactant index.

Temperature (°C)	Concentration (M)	Corrosion Rate (× 10^{-3}mg/cm hr)	Inhibition efficiency (%)	Surface Coverage
	Blank	5.61	.	
	2 × 10^{-3}	3.53	37.01	0.3701
	4 × 10^{-3}	2.66	52.55	0.5255
30°C	6 × 10^{-3}	1.14	79.62	0.7962
	8 × 10^{-3}	0.7	88.05	0.8805
	10 × 10^{-3}	0.34	93.87	0.9387
	Blank	5.98	...	...
	2 × 10^{-3}	3.99	33.33	0.3333
60°C	4 × 10^{-3}	3.34	44.12	0.4412
	6 × 10^{-3}	2.91	48.72	0.4872
	8 × 10^{-3}	2.24	62.58	0.6258
	10 × 10^{-3}	1.69	71.77	0.7177

Table 2: Calculated values of corrosion rate (CR), surface coverage (Θ) and Inhibition Efficiency (% IE) of aluminium corrosion in different concentration of Nivaquine at 30°C and 60°C.
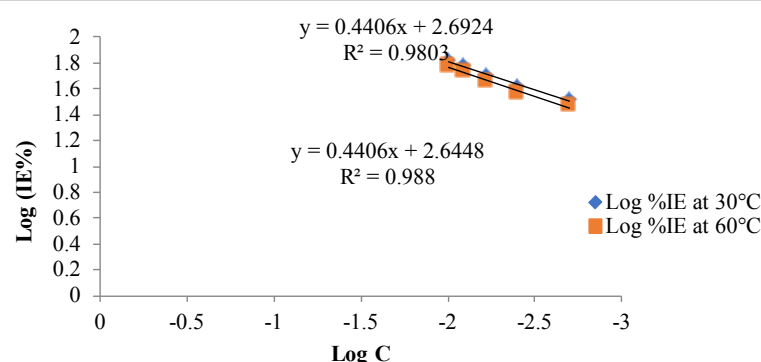
Figure 3: Freundlich adsorption isotherm plot as log (% IE) versus log C for aluminium coupons in 1 M HCl solution containing different concentration of Amodaquine.
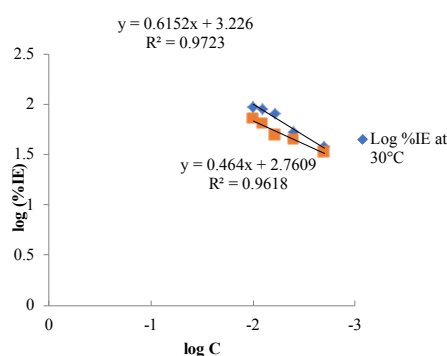
Figure 4: Freundlich adsorption isotherm plot as log (% IE) versus log C for aluminiumcoupons in 1 M HCl solution containing different concentration of Nivaquine.

$$\chi = -\frac{1}{2}\left[E_{LUMO} + E_{HOMO}\right] \qquad (4)$$

$$\eta = \frac{1}{2}\left[E_{LUMO} - E_{HOMO}\right] \qquad (5)$$

$$\sigma = \frac{1}{\eta} \qquad (6)$$

Results and Discussion

Effect of inhibitor concentration

The corrosion parameters obtained by weight loss measurement for aluminium in the absence and presence of different concentrations of the inhibitors in 1 M HCl at different temperatures are tabulated in Tables 1 and 2 for Amodaquine and Nivaquine respectively. As seen from the table, the increase in the concentration of the inhibitors afforded decrease in the corrosion rate values while inhibition efficiency increased. The decrease with the rise in temperature, indicate that at higher temperature, dissolution of aluminium predominates on the surface. This effect can be explained by the decrease in the strength of the adsorption process at high temperature; suggesting physical adsorption [11]. The inhibition efficiency and surface coverage were found to be higher in Nivaquine whereas the corrosion rate was observed to be higher in Amodaquine.

Adsorption isotherm and thermodynamic parameters

Adsorption isotherm study describes the adsorptive behavior of organic inhibitors which explains the adsorption mechanism. Two types of adsorption may be distinguished i.e., physical and chemical.

However, which predominates over the other is detected from the temperature studies. Physisorption predominates if inhibition efficiency decreases with increase in temperature. Hence, it can be concluded that in the adsorption of the inhibitors, it is the physisorption which predominates because Inhibition efficiency decreased with increase in temperature. Furthermore, a plot of log (%IE) vs log C gives a straight line indicating Freundlich adsorption isotherm (Figures 3 and 4). The correlation coefficient R^2 was used to choose the isotherm that best fit experimental data. The Freundlich adsorption isotherm was found to be the best description of the adsorption behaviour of the studied inhibitor on the aluminium surface as the correlation coefficient were 0.980 at 30°C and 0.988 at 60°C for Amodaquine and 0.972 at 30°C and 0.961 at 60°C for Nivaquine with a negligible deviation of the slope from unity. According to this isotherm, the inhibition efficiency (%IE) is related to the equilibrium adsorption constant K_{ads} and the inhibitor concentration C according to the equation:

$$\%IE = KC^n \tag{7}$$

Where $0 < n < 1$, or

$$\log \%IE = \log K_{ads} + n \log C \tag{8}$$

The free energy of adsorption ΔG°_{ads} calculated using the equation below, is presented in Table 2.

$$\Delta G^\circ_{ads} = -RT \ln(55.5 K_{ads}) \tag{9}$$

Where R is the molar gas constant, T is the absolute temperature and 55.5 is the concentration of water in solution in mol^{-1} [12].

The value of ΔG°_{ads} of the inhibitor was found to be -25.733 kJ/mol at 30°C and -27.975 kJ/mol at 60°C for Amodaquine and -28.83 kJ/mol at 30°C and -28.714 kJ/mol at 60°C for Nivaquine (Table 3). The negative value of ΔG_{ads} indicated spontaneous adsorption of the inhibitor on the aluminium surface. From the result, Nivaquine spontaneously adsorbs more than Amodaquine. Generally, the magnitude of ΔG_{ads} -20 kJ/mol or less negative indicates electrostatic interactions between inhibitor and the charged metal surface (i.e., physisorption). Those around -40 kJ/mol or more negative are indicative of charge sharing or transferring

from organic species to the metal surface to form a coordinate type of metal bond (i.e., chemisorptions) [13]. In the present work, the calculated values of ΔG° at 303 K for aluminium is -25.733 kJ/mol and -28.83 kJ/mol, which indicate that adsorption of the inhibitor on the aluminium surface involves physical process [14-16]. The inhibition efficiency decreased with increasing temperature indicating inhibitor adsorbed predominantly physically on the surface of mild steel. The efficiency of an organic compound as corrosion inhibitor depends not only on the characteristics of the environment in which it acts, the nature of the metal surface and electrochemical potential at the interface, but also on the structure of the inhibitor itself, which includes the number of adsorption active centers in the molecule, their charge density, the molecule size, the mode of adsorption, the formation of metallic complexes and the projected area of the inhibitor on the metallic surface.

Effect of temperature

The effect of temperature on the corrosion rate of aluminium in 1 M HCl solution in the absence and presence of different concentrations of the inhibitors were studied at 30°C and 60°C by weight loss measurements. The data in Tables 1 and 2 shows that the % IE decreases as the temperature increases and with decrease in concentration of studied inhibitors.

In acidic solution, the corrosion rate is related to temperature by Arrhenius equation.

$$\text{Log CR} = \log A - E_a/2.303RT \tag{10}$$

Where CR, is the corrosion rate determined from the weight loss measurement. E_a, the apparent activation energy. A, the Arrhenius constant. R, the molar gas constant and T, the absolute temperature.

The values of activation energies were calculated and given in Table 4. These values indicated that the presence of both inhibitors generally increases the activation energy of metal dissolution. The adsorption of the studied inhibitors is assumed to occur on the higher energy sites and the presence of the inhibitor, which results in the blocking of the

Inhibitor	Temperature (°C)	Adsorption		Parameter		
		K_{ads}	ΔG_{ads} (kJ/mol)	Slope	R^2	Intercept
Amodaquine	30	492.04	-25.733	0.44	0.98	2.692
	60	440.55	-27.975	0.44	0.99	2.692
Nivaquine	30	1682.7	-28.83	0.615	0.97	3.226
	60	638.26	-28.714	0.464	0.96	2.760

Table 3: Adsorption parameters from Freundlich Isotherm for Aluminium coupons in 1 M HCl containing different concentrations of the inhibitors at 30°C and 60°C.

Inhibitor	Concentration (M)	Activation			Parameter
		E_a (kJ/mol)	A	ΔH (kJ/mol)	ΔS (kJ/mol K)
Amodaquine	Blank	1.7864	0.0114	-0.8545	-291.03
	2×10^{-3}	3.3689	0.0143	0.7282	-236.09
	4×10^{-3}	3.5754	0.0136	0.9348	-232.09
	6×10^{-3}	4.4106	0.0162	1.7703	-230.67
	8×10^{-3}	5.7919	0.0225	3.1515	-227.92
	10×10^{-3}	7.2456	0.033	4.6049	-223.56
Nivaquine	Blank	1.7864	0.0114	-0.8545	-291.03
	2×10^{-3}	3.426	0.0137	0.7855	-232.02
	4×10^{-3}	6.367	0.0333	3.7265	-224.67
	6×10^{-3}	26.211	37.538	23.57	-166.22
	8×10^{-3}	32.532	283.3	29.891	-149.42
	10×10^{-3}	44.85	18264	42.209	-114.77

Table 4: Activation parameters from Arrhenius and Transition state Equations for the rate of corrosion of aluminium coupons in 1 M HCl solution containing different concentration of Amodaquine and Nivaquine.

active sites, must be associated with an increase in the activation energy of aluminium corrosion in the inhibited state. The higher values of E_a in the presence of inhibitors compared to that in the absence and the decrease in the IE% with rise in temperature is interpreted as physisorption [17]. The values of the enthalpy of activation $\Delta H°$ and
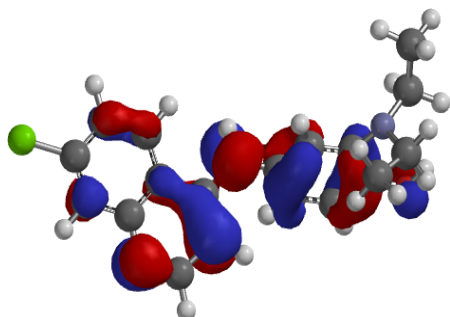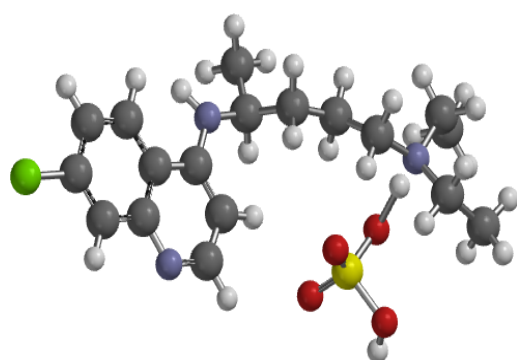

Figure 5: Frontier Molecular Orbital Diagram (HOMO) of Amodaquine.
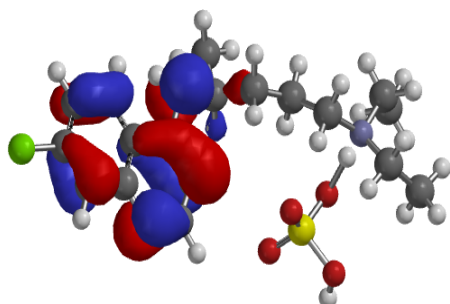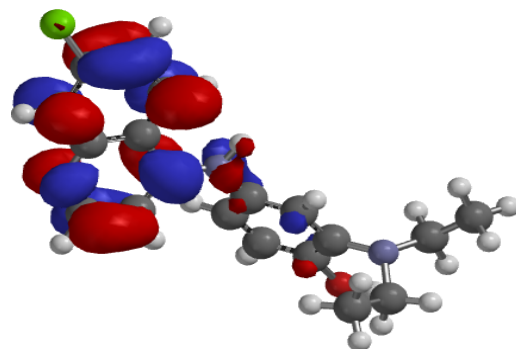

Figure 6: Frontier Molecular Orbital Diagram (HOMO) of Nivaquine.
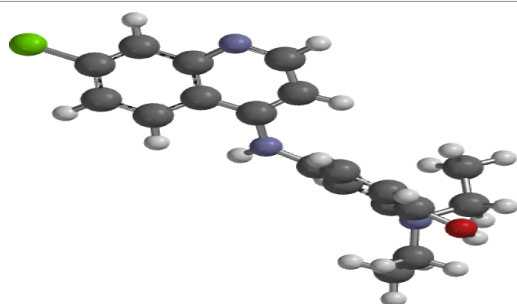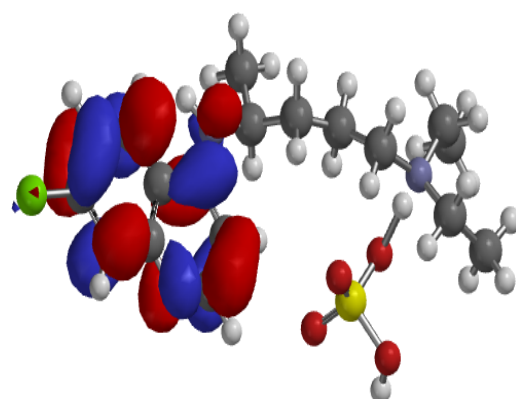

Figure 7: Optimized structure of Amodaquine.

Figure 8: Optimized structure of Nivaquine.

Figure 9: Frontier Molecular Orbital Diagram (LUMO) of Amodaquine.

Figure 10: Frontier Molecular Orbital Diagram (LUMO) of Nivaquine.

the entropy of activation $\Delta S°$ were obtained from the transition state equation:

$$CR=(RT/Nh) \exp (\Delta S°/R) \exp- (\Delta H°/RT) \qquad (11)$$

Where h, is the Planck's constant, N; is the Avogadro's number; T, is the Absolute temperature and R is the molar gas constant. Plots of log (CR/T) as a function of 1/T (Figures 5 and 6) were made and straight lines were obtained. $\Delta H°$ and $\Delta S°$ were computed from the slope and intercept respectively from the linear plots. The computed values of the thermodynamics parameters of activation for the dissolution of aluminium at different temperature are presented in Table 4. Examination of these data reveals that the values of $\Delta H°$ and $\Delta S°$ in the presence of the additives increase over that of the uninhibited solution. This implies that the energy barrier of the corrosion reaction in the presence of inhibitors increased, which is expected. The value of $\Delta H°$ and $\Delta S°$ for the inhibited is more than of the uninhibited. The positive values of $\Delta H°$ show the endothermic nature of the process in the inhibited system. $\Delta S°$ is positive, meaning that a decrease in disorderliness takes place in going from reactants to the activated complex.

Quantum descriptors

Quantum-chemistry calculations have been performed in order to study the molecular structure and the reaction mechanisms to interpret the experimental results as well as to solve chemical ambiguities and to correlate the inhibition efficiency to the molecular properties of inhibitor. The optimized geometry of the inhibitors as well as the nature of their molecular orbitals, HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) are shown

Quantum Parameter	Amodaquine	Nivaquine
EHOMO (eV)	-5.82	-5.52
ELUMO (eV)	-1.73	-1.02
Egap (eV)	4.09	4.5
Softness	0.489	0.444
Absolute hardness	2.045	2.25
Absolute electronegativity	3.775	3.27
CPK PSA	34.659	86.566
Dipole moment (Debye)	6.54	14.22
Polarizability	68.57	73.36

Table 5: Quantum parameters for Amodaquine.

in Figures 5-10. According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of reactants [18]. The energy of the HOMO is directly related to the ionization potential and the energy of the LUMO is directly related to the electron affinity. The HOMO-LUMO gap, i.e., the difference in energy between the HOMO and LUMO, is an important stability index [19]. A large HOMO-LUMO gap implies high stability for the molecule in chemical reactions [20]. The concept of activation hardness has been also defined on the basis of the HOMO-LUMO energy gap. The qualitative definition of hardness is closely related to the polarizability, since a decrease of the energy gap usually leads to easier polarization of the molecule [21].

Quantum chemical parameters related to the molecular electronic structure such as, E_{HOMO}, E_{LUMO}, energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$) and the dipole moment (μ), total energy (TE), absolute hardness (η), absolute electronegativity (χ), and softness (σ) were calculated. It is found that, high E_{HOMO} values of the inhibitors led to higher electron donating ability to appropriate acceptor molecules with low energy empty molecular orbitals. Low E_{LUMO} value of the inhibitors suggests that it accept electrons easily from donor molecules. The difference in energy, E_g, is the energy required to move an electron from HOMO to LUMO. The smaller value of E_g of the inhibitors facilitates adsorption of the molecule and thus will cause higher inhibition efficiency, because the energy to remove an electron from the last occupied orbital will be low. A hard molecule has a large energy gap and a soft molecule is associated with a small energy gap. Therefore, soft molecules are more reactive than hard molecule [22,23]. The most widely used quantity to describe the polarity is the dipole moment of the molecule [24]. The dipole moment (μ) and Polarizability for Nivaquine was found to be higher than that of Amodaquine, this favoured greater accumulation of Nivaquine molecules on the metallic surface; the Polar surface area according to Table 5 implies that it has a good inhibitive potential.

Excellent corrosion inhibitors are usually those organic compounds that not only donate electrons to unoccupied orbital of the metal surface but also accept free electrons from the metal [25].

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