Nigerian Journal of Pharmaceutical and Applied Science Research, 8(2): 89-102 May 2019 (ISSN 1485-8059   Available at www.nijophasr.com

Experimental and Quantum Chemical Studies on the Corrosion Inhibition potential of β-Carotene for Mild Steel in Solution of HCl

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ABSTRACT

The study was designed to investigate the corrosion inhibition potential of beta carotene for mild steel in acidic medium. Gravimetric, gasometric and polarization methods were used for the study. The results obtained indicated excellent corrosion efficiencies from all the used monitoring methods. Correlation between results obtained from different methods were also excellent. Carotene acted as an adsorption inhibitor. Its adsorption is exothermic, spontaneous and reflected physiosorption adsorption mechanism. Langmuir and Temkin adsorption isotherms best fitted the adsorption characteristics of the inhibitor. Computational chemistry investigation revealed semi empirical values that compares favourably with those of excellent corrosion inhibitors. The sites for electrophilic and nucleophilic attacks resided in the C(35) and C(14) atoms respectively.

Key words: Corrosion .metal, Green inhibition, beta carotene

INTRODUCTION

The use of metals and metallic alloys in industrial manufacturing as well as several industrial fabrications (such as pipelines, etc) is on the increase and the need to continuously research for methods of preventing their degradation through corrosion is also growing. Corrosion of metals is a serious industrial and environmental problems because it returns metals to their natural state (Eddy *et al*., 2018). Several measures have been proposed for reducing the rate of corrosion of metals including electroplating, oiling, painting, galvanization, anodic/cathodic protection, etc. However, the use of inhibitors has been generally accepted as the most effective measure especially in corrosion of pipelines and other metals use in transporting fluids (Eddy *et al*., 2015). Corrosion inhibitors are compounds that retard the rate of corrosion of metals when added to the corrosive medium in minute concentration. The major problem in the corrosion industrial is the choice of inhibitors that is less, expensive, biodegradable and eco-friendly. These requirements are highly met by most effective inorganic compounds hence, in recent times, remediation effort is centred on the use of organic compounds including plant or animal extracts (Eddy *et al*., 2010). However, from chemical point of view some of the plants extract suffer from the inability to know the actual chemical structure/structures that are involved in the corrosion inhibition process. Therefore, it becomes necessary to search for compounds whose structure and predictive properties are well established. The present study is aimed at using beta carotene for the inhibition of mild steel corrosion in solution of HCl. The chemical structure of beta carotene is shown below,

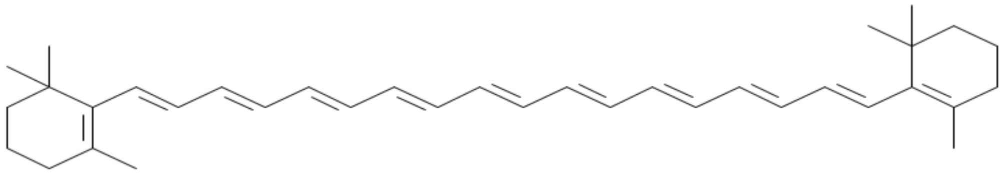

Figure 1:   Chemical structure of β carotene

Available literature reveals that organic compounds that are long chain, aromatic and that have hetero atoms or pi bonds are likely effective corrosion inhibitors. Since the chemical structure of β-carotene fulfilled these conditions, it is significant to investigate its corrosion inhibition efficiency. Literature is scanty on the use of carotene for the inhibition of mild steel corrosion. However, Badawy and El-Rabiel (2014) studied the stability of Cu-Al-Ni alloys used in the manufacture of NaCl in sulfide polluted chloride solutions. Three different alloys, namely, Cu-10Al-5Ni, Cu-10Al-10Ni and Cu-10Al-45Ni were investigated in chloride containing sulfide$^-$ions using different electrochemical techniques

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including polarization and electrochemical impedance spectroscopy. The presence of sulfide ions in the chloride solution accelerates the corrosion of Cu-Al-Ni alloys, whereas the increase of the nickel content in the alloy improves its corrosion resistance. β-carotene as eco-friendly corrosion inhibitor was used to protect the Cu-10Al-Ni alloys from corrosion in presence of sulfide ions. The corrosion inhibition efficiency reached >95% at 50 ppm concentration of β -carotene. The alloy surface was investigated by the scanning electron microscope and the surface constituents were analyzed by EDAX. Saldo *et al*. (1990) has also implicated carotene as one of the major components that are responsible for the inhibitory properties of naturally occurring corrosion inhibitors for most natural product. De Santana *et al*. (2015) also reported that carotenoid was effective synergistic component towards the inhibition of the corrosion of carbon steel by biodiesel. The present study is aimed at investigating the inhibition potential of beta carotene for mild steel corrosion in acidic medium.

MATERIALS AND METHODS

Materials used for the study were mild steel sheet of composition (wt %, as determined by quantiometric method) Mn (0.6), P (0.36), C(0.15) and Si (0.03) and Fe (98.86). The sheet was mechanically press cut into different coupons, each of dimension, 3x2x0.12 cm for weight loss studies and 1x1mm for electrochemical study. The coupons were wet polished with different grades of SiC abrasive paper (#400 to #1200), degreased by washing with ethanol, cleaned with acetone and allowed to dry in the air before preservation in a desiccator. All reagents used for the study were analar grades and double distilled water was used for their preparation. Concentrations of HCl used for weight loss and polarization studies were 0.1 M and 0.5 M respectively. Concentrations of the inhibitor were within the range, 0.1 to 0.5 g/L

Gravimetric method

In the gravimetric experiment, a previously weighed metal (mild steel) coupon was completely immersed in 250 ml of the test solution in an open beaker. The beaker was covered with aluminium foil and inserted into a water bath maintained at 303 K. After every 24 hours, the corrosion product was removed by washing each coupon (withdrawn from the test solution) in a solution containing 50 % NaOH and 100 g l^{-1} of zinc dust. The washed coupon was rinsed in acetone and dried in the air before re-weighing. The experiment was repeated at 333 K for 168 hours. In each case, the difference in weight for a period of 168 hours was taken as the total weight loss. From the average weight loss (mean of three replicate analysis) results, the inhibition efficiency (%I) of the inhibitor, the degree of surface coverage (θ) and the corrosion rate of mild steel (CR) were calculated using equations 1 to 3 respectively (Eddy and Ebenso, 2010);

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

$$\theta = \left(1 - \frac{w_1}{w_2}\right) \qquad 2$$

$$CR = \frac{\Delta w}{At} \qquad 3$$

where w_1 and w_2 are the weight losses (g) for mild steel in the presence and absence of the inhibitor, θ is the degree of surface coverage of the inhibitor, $\Delta w = w_2 - w_1$, A is the area of the mild steel and aluminium coupon (in cm^2), t is the period of immersion (in hours) and W is the weight loss of mild steel and aluminium after time, t.

Gasometric method

In gasometric study, test solution (different concentrations of halides, inhibitor, acid or their mixtures) was poured into the reaction vessel. Upon the introduction of mild steel, the flask was quickly corked and the rise in volume of the paraffin due to hydrogen evolution was noted after every minute until a steady volume was observed. From gasometric measurements, the inhibition efficiency was calculated using equation 4:

$$\%I = \left(\frac{V_{H_2}^0 - V_{H_2}}{V_{H_2}}\right) \times \frac{100}{1} \qquad 4$$

Polarization method

Linear polarization studies were carried out at a potential range of ± 250 mV for mild steel versus corrosion potential at a scan rate of 0.33 mV/s at 303K . Each test was run in triplicate. Measurements were performed in 0.1 M HCl and containing various concentration of the test inhibitors. The potentiodynamic polarization sweeps were conducted at a sweep rate of 0.5 mV/s. The solution and metal coupon were changed after each sweeps.

For each experimental condition, two to three measurements were performed to estimate the repeatability. The repeatability was quite good, and the changes observed in the results reflect influences of various parameters beyond the experimental error.

Computational and Theoretical Considerations

All computational softwares were provided by Prof. Nnabuk Okon Eddy of the Department of Pure and Industrial Chemistry, University of Nigeria, Nsukka. Quantum calculations were carried out using Restricted Hartree-Fock (RHF) level and AM1 semi-empirical SCF-MO methods in the MOPAC 2000 program of CS ChemOffice packet program version 8 for Windows. Calculations were performed on an IBM compatible Intel Pentium IV 2.8 GHz computer. All quantum theoretical calculations were carried out without any geometry constraints for full geometry optimizations using the program default calculation setting.

Geometry optimization was achieved by first drawing the structure of beta carotene using Ultra Chem3D programme in the Chem office suite. The structures were optimized by successively optimizing with MM+, PM6 and DFT (B3-YLP) until the gradient was 0.0. The input programmes (input file) for all computational calculations were developed by by the major supervisor. Single point energy calculations were carried out using AM1, PM6, PM3, MNDO and RM1 Hamiltonians in the MOPAC 2008 software for Windows. Calculations were performed on an HP compatible Intel Pentium V (4.0 GHz, 4 GB RAM) computer. The following quantum chemical indices were calculated (for gas and aqueous phases): the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the dipole moment (μ), the total energy (TE), the electronic energy (EE), the ionization potential, the cosmo area (cosAr) and the cosmo volume (CosVol). The Muliken charges (q) for nucleophilic and electrophilic attacks were computed using GAMESS and Hyperchem computational softwares. The programme setting for the GAMES calculations (DFT) were; Corelation.: MP2, correlation type: B3YLP, Basis set: STO3G but for DFT calculations (using Hyperchem release 8.0.2) esxchange correlation was set to B3-LYP, while orbital basis set was set at STO3G. The programme was run for 50 iterations, 100 cycles and convergence limit of 1 x 10^{-5}.

RESULTS AND DISCUSSIONS

Gravimetric and gasometric methods

Fig. 1 present plots for the variation of volume of hydrogen gas evolved with time during the corrosion of mild steel in 3 M HCl containing various concentrations of β- carotene at 303 K. It is interesting to note that when mild steel corrodes in HCl, hydrogen gas would be evolved according to the following equation:

$$3Fe_{(s)} + 3HCl_{(aq)} \rightarrow FeCl_{3(aq)} + 3H_{2(g)} \qquad 5$$

Equation 1 revealed that the rate of corrosion of mild steel in 3 M HCl can be monitored by measuring the volume of hydrogen gas evolved. This is the basic principle of gasometry experiment. From the plots, it can be seen that the volumes of hydrogen gas evolved by the blank in both cases are greater than the volume of hydrogen gas evolved, in the presence of the inhibitors. This indicates that β- carotene retarded the corrosion of mild steel in solution of HCl. It is also evident from the plots that the rate of evolution of hydrogen gas decreases with increase in the concentration of the inhibitor, which suggests that β- carotene are adsorption inhibitors for mild steel corrosion. Adsorption inhibitors act through the mechanism of physical or chemical adsorption and are characterised by increase in inhibition efficiency with concentration (Ameh and Eddy, 2014). Values of inhibition efficiencies of β-carotene are presented in Table 1. The results obtained indicated that the inhibition efficiency of β-carotene ranged from 45.00 to 74.49 %.

Fig. 2 shows plots for the variation of weight loss of mild steel with time for the corrosion of mild steel in 0.1 M HCl containing various concentrations of β-carotene at 303 and 333 K.

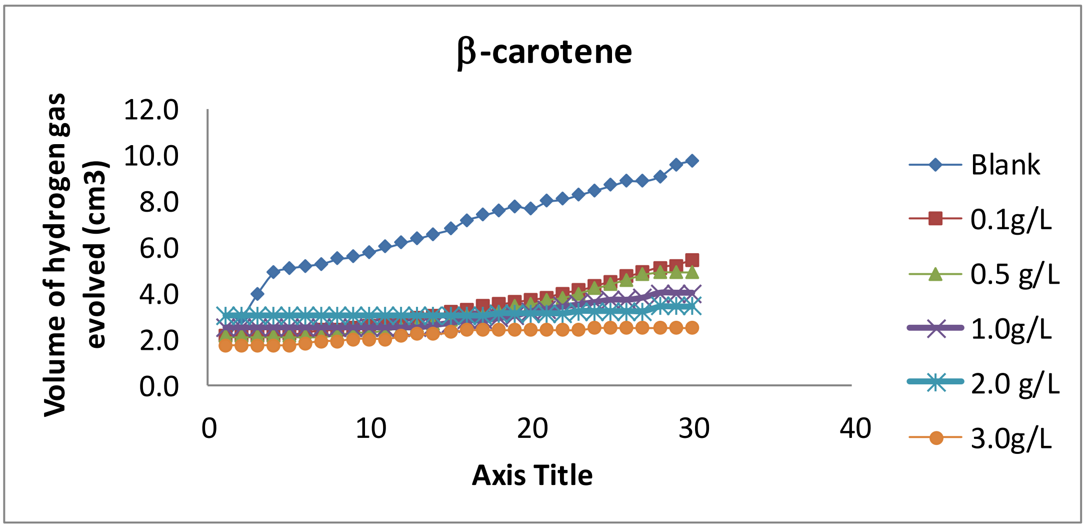
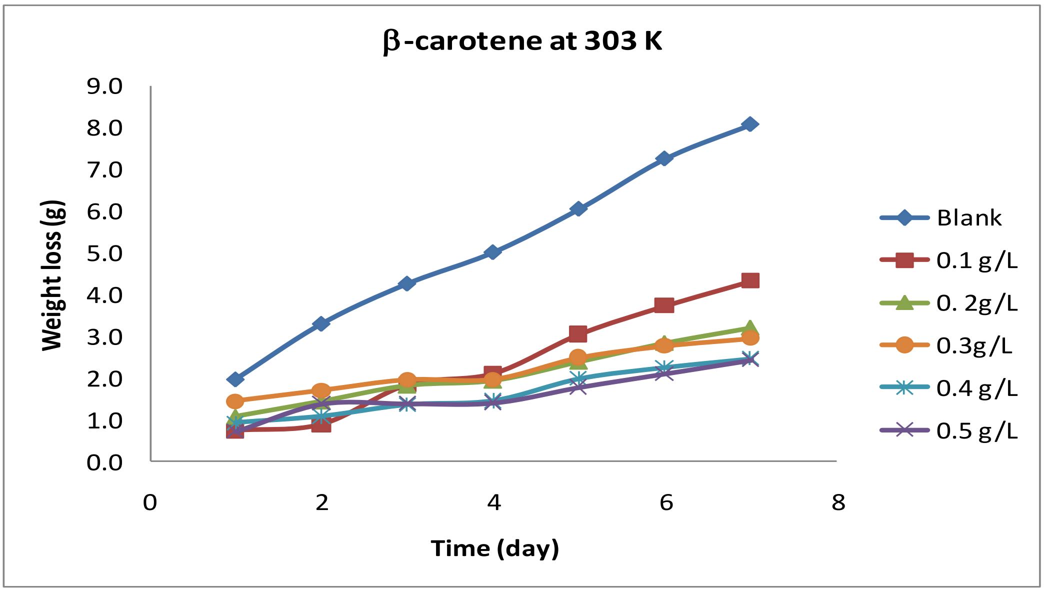


Fig. 2: Variation of volume of hydrogen gas evolved with time for the corrosion of mild steel in 3 M HCl containing various concentrations of beta carotene at 303 K

Table 1: inhibition efficiencies of β- carotene

C (g/L)	Volume of H_2 gas evolved (cm^3)	Inhibition efficiency (%)
Blank	9.8	
0.1	5.4	45.00
0.2	4.9	50.00
0.3	4.0	59.18
0.4	3.4	65.31
0.5	2.5	74.39

From the plots, it is evident that weight loss of mild steel in solute ions of HCl increases with time but decreases with increasing concentration of β-carotene indicating that the rate of corrosion of mild steel in solutions of HCl is retarded by the presence of β-carotene (Uwah *et al*., 2013e).



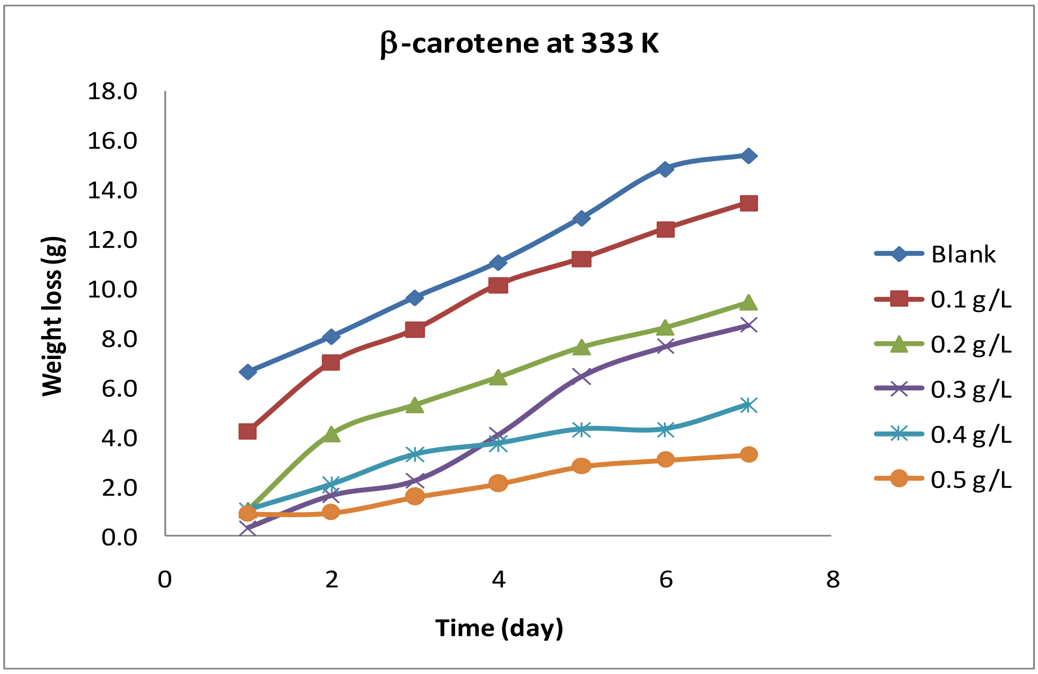


Fig 2: Variation of weight loss with time for the corrosion of mild steel in 0.1 M HCl containing various concentrations of β-carotene at 303 and 303 K

This also implies that β-carotene inhibited the corrosion of mild steel in solutions of HCl. Comparison of the plots at 303 K with the one at 333 K revealed that weight loss of mild steel increases with increase in temperature indicating that the corrosion rate of mild steel in solutions of HCl increases with increase in temperature. This also implies that the inhibition efficiency of the inhibitors will decrease with increase in temperature.

Table 2: Corrosion rate of mild steel in solutions of HCl and inhibition efficiencies of various concentrations of β-carotene for mild steel in 0.1 M HCl

C (g/L)	**Corrosion rate ($g/h^{-1}cm^{-2}$) x 0.001**		**Inhibition efficiency *%IE)**	
	303 K	333 K	303 K	333 K
Blank	2.41	4.58		
0.1	1.29	4.01	49.71	13.39
0.2	0.95	2.82	62.42	39.17
0.3	0.88	2.54	65.24	45.25
0.4	0.74	1.58	70.62	65.92
0.5	0.73	1.45	71.02	68.69

Values of inhibition efficiencies of β-carotene obtained from gasometric, and gravimetric methods are presented in Tables 1 and 2 respectively. The results obtained generally revealed that the inhibition efficiency increases with increase in concentration, confirming that beta carotenoids is an adsorption inhibitor. The inhibition efficiencies were also found to decrease with increasing temperature, which implies that the extent of adsorption also decreases with increase in temperature. Hence both inhibitors acted through the mechanism of physical adsorption, which involves charge transfer from charged inhibitor to charged metal surface.

Comparison of the results obtained from gasometric and gravimetric experiments indicated that the two results are in agreement with each other and gave excellent correlation as indicated by calculated value of degree of linearity (R^2 = 0.9550).

Polarization study

Linear polarization resistant (LPR) and potentiometric polarization resistant (PPR) studies were also conducted during the study. From PPR study, plots obtained for the variations of applied potential with log(current) for corrosion of mild steel in the absence and presence of β-carotene are presented in Fig. 3. Each of the plots consists of cathodic and anodic arms, as well as a plateau. The displacement shown by the cathodic and anodic arms of the plots seems to be extended for all the plots. Polarization data deduced from the plots are presented in Table 3. The results show corrosion current and the corresponding corrosion potential. From the corrosion current, the inhibition efficiency of the respective inhibitor was calculated using the following equation (Okafor and Zheng, 2009):

$$\%I = \frac{i^0_{Corr} - i_{Corr}}{i^0_{Corr}} \times \frac{100}{1} \qquad 6$$

where i^0_{Corr} and i_{Corr} are the uninhibited and inhibited corrosion current densities, respectively. Calculated values of %I for the various concentrations of β-carotene are also presented in Table 4. On the other hand, values of polarization resistant obtained from linear polarization study are presented in Table 5. From the R_p values, the corrosion inhibition efficiencies of β-carotene were calculated using the following equation,

$$\%I = \frac{R_{p(Inh)} - R_p}{R_{p(Inh)}} \times \frac{100}{1} \qquad 7$$

where R_p and $R_{p(inh)}$ are the uninhibited and inhibited polarization resistance, respectively. Calculated values of %I obtained from equation 3 are also presented in Table 5.

Potentiodynamic polarization (PDP) and linear resistant polarization (LRP) were carried out simultaneously. The results obtained from both methods are in good agreement, exhibiting R^2 values of 0.9170 and 0.8777 for β-carotene. These values also show appreciable correlation with data obtained from weight loss measurements. From Fig. 3, it can be seen that the addition of β-carotene is seen to affect both the cathodic and anodic partial reactions, thereby reducing the cathodic and anodic current densities and the corresponding corrosion densities. This indicates that β-carotene is a mixed type inhibitor in 0.1 M HCl. From potentiometric plots, there is no evidence of passive film formation on the surface of mild steel, in the presence or absence of the inhibitors. However, values of corrosion potentials (E_{Corr}) and corrosion current (i_{Corr}) were observed to decrease with increase in the concentration of the inhibitors indicating that β-carotene are adsorbed on the surface of the mild steel. Generally, there are three basic modes, through which organic compounds inhibit the corrosion of metals. These include geometric blocking through the adsorption of the inhibitor, active sites blocking by the adsorbed inhibitor and electro-catalytic effect of the inhibitor or its reaction products. From the polarization results, it can be inferred that β-carotene acted via geometric blocking effect.

Table 3: Potentiodynamic polarization resistant data for the corrosion of mild steel in 0.1 M HCl containing various concentrations of β-carotene at 303 K

Conc.(g/l)	**E_{corr} (mV)**	**I_{corr} (μA)**	**IE %**	**R_p (Ω/cm^2)**	**%IE**
	PDP			LPR	
Blank	-864.95	1179.0	-	17.32	-
0.1	-869.38	516.46	56.19	53.22	67.46
0.2	-934.37	343.09	70.89	69.23	74.98
0.3	-952.04	286.53	75.69	83.99	79.38
0.4	-1109.5	187.68	84.08	130.41	86.72
0.5	-1223.4	128.56	89.09	806.50	97.85

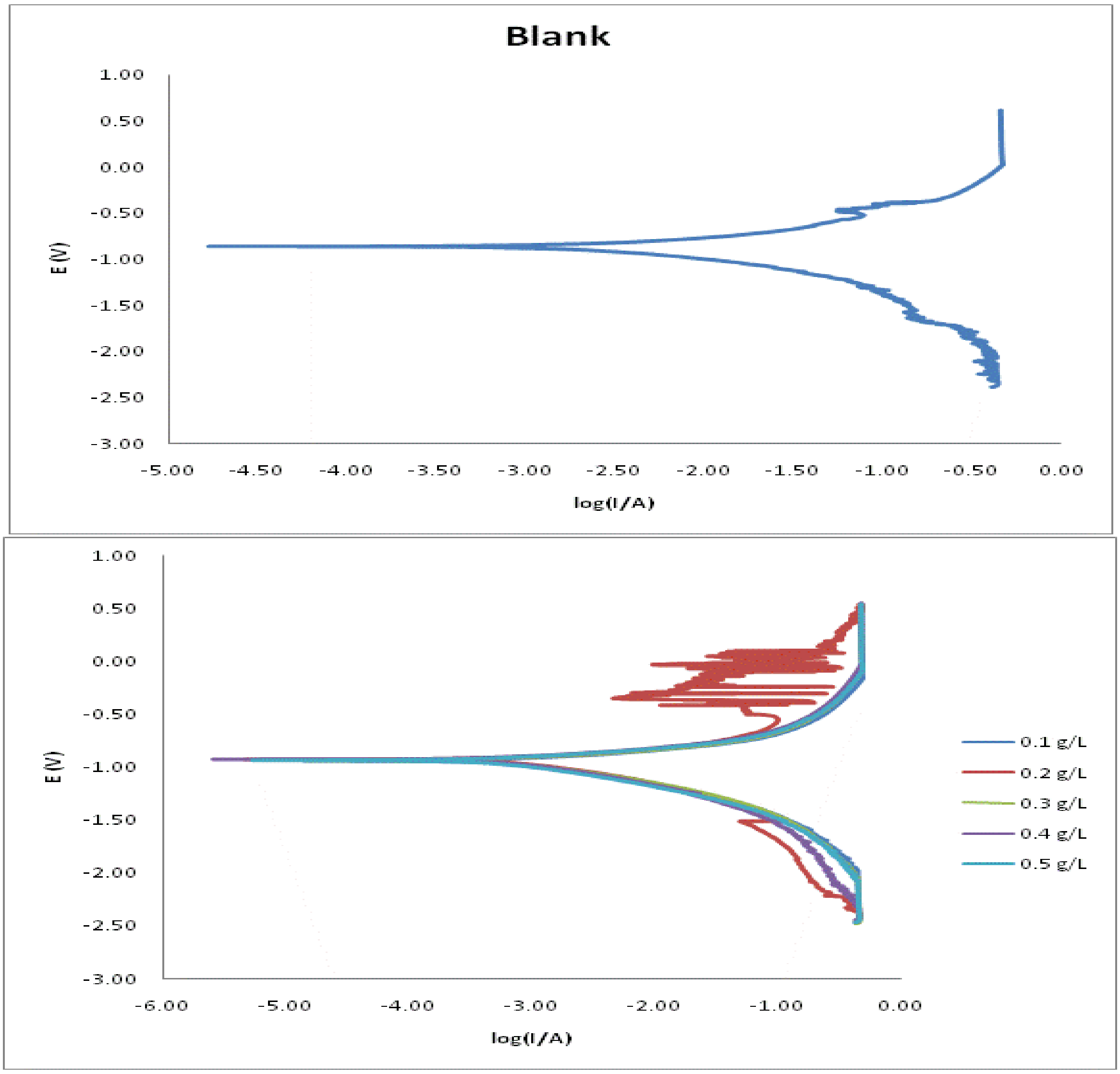


Fig. 3: Potentiodynamic plots for the corrosion of mild steel in 0.1 M HCl containing various concentrations of β-carotene

Effect of temperature

Every chemical reaction (including corrosion) requires a minimum energy before it can proceed. This minimum energy is called activation energy and represent the threshold energy required for corrosion of mild steel. In this study, the activation energies at various concentrations of the inhibitors were calculated using the Arrhenius equation, which can be written as follows (Uwah et al., 2013a)

$$CR = Aexp\left(\frac{-E_a}{RT}\right) \qquad 8$$

where CR is the corrosion rate of mild steel, A is the Arrhenius or pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T is the temperature. If we consider the corrosion rates at two temperatures (i.e CR_1 and CR_2 corresponding to T_1 and T_2 respectively), then equation 8 can be simplified to equation 9, as shown below,

$$\frac{CR_2}{CR_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad 9$$

Values of the activation energy calculated from equation 6 for both inhibitors are presented in Table 4. The activation energies ranged from 29.71 to 32.40 kJ/mol and from 19.42 to 31.84 kJ/mol for β-carotene respectively. These values are within the limit expected for the mechanism of physical adsorption. Therefore the adsorption of β-carotene on the surface of mild steel support the mechanism of physical adsorption. It can also be deduced from Table 4 that the activation energy for the blank (i.e 0.1 M HCl) is lower than those calculated for the inhibited system, which indicated that the corrosion of mild steel in solution of HCl is retarded by β-carotene.

Table 4 Heat of adsorption and activation energy for the adsorption of β-carotene on mild steel surface

C(g/L)	**E_a (kJ/mol)**	**Q_{ads} (kJ/mol)**
Blank	18.04	
0.1	31.84	-38.92
0.2	30.40	-19.88
0.3	29.73	-17.20
0.4	21.39	-4.56
0.5	19.42	-2.32

Thermodynamic/adsorption considerations

The heat of adsorption of the inhibitor unto mild steel surface was calculated using the following equations (Uwah et al., 2013b)

$$Q_{ads} = 2.303R\left(\frac{\theta_2}{1-\theta_2} - \frac{\theta_1}{1-\theta_1}\right) \times \left(\frac{T_1T_2}{T_2 - T_2}\right) \qquad 10$$

where Q_{ads} is the heat of adsorption, R is the gas constant, θ_1 and θ_2 are the degrees of surface coverage of the inhibitor at the lower and higher temperatures (T_1 and T_2) respectively. Calculated values of Q_{ads} are also presented in Table 4. These values are low and negative, indicating that the adsorption of the inhibitors is exothermic and that the mechanism of physical adsorption is favoured. Physical adsorption is characterised by low values of heat of adsorption, as found in the present study. Values of Q_{ads} calculated from equation 10 are also seen to decrease with increase in the concentration of the inhibitor indicating that the adsorption becomes more exothermic with increasing concentration of the inhibitor.

Adsorption isotherm

Adsorption isotherm is significant in analysing the adsorption behaviour of an inhibitor. The general form of adsorption isotherm equation is given as follows (Eddy and Odiongenyi, 2010)

$$f(\theta, x)\exp(2a\theta) = Cb_{ads} \qquad 11$$

where $f(\theta, x)$ is the configurational factor which depend on the physical model and the assumption underlying the model, x is the size ratio, 'a' is the molecular interaction parameters, C is the concentration of the inhibitor in the bulk electrolyte and b_{ads} is the equilibrium constant of adsorption.

In this work, adsorption data obtained from gravimetric study were used to test for the isotherm that best describes the adsorption of β-carotene at various temperatures. The test revealed that the Langmuir adsorption model fitted the adsorption of of β-carotene at 303 K and 333 K respectively. The Langmuir adsorption model is based on the assumptions expressed by equation 9 and it rests perfectly, when there is a unit slope, signifying the absence of molecular interaction between the adsorbed species (Uwah *et al.*, 2013c)

$$ln\left(\frac{C}{\theta}\right) = lnb_{ads} - lnC$$

12

Furthermore, the basic assumptions governing the Langmuir adsorption model are as follows,

The available adsorption sites on the metal is fixed and each site holds a fixed number of adsorbate

The standard free energy change is the same for all the adsorption sites and is independent of the value of degree of surface coverage

The adsorbate do not interact with another, indicating that there is no effect of lateral interaction on the standard free energy change

From equation 12, a plot of $ln\left(\frac{C}{\theta}\right)$ versus ln(C) should be a straight line with slope and intercept equal to unity and lnb_{ads} respectively. Fig 4 shows the Langmuir isotherms for the adsorption of β-carotene.

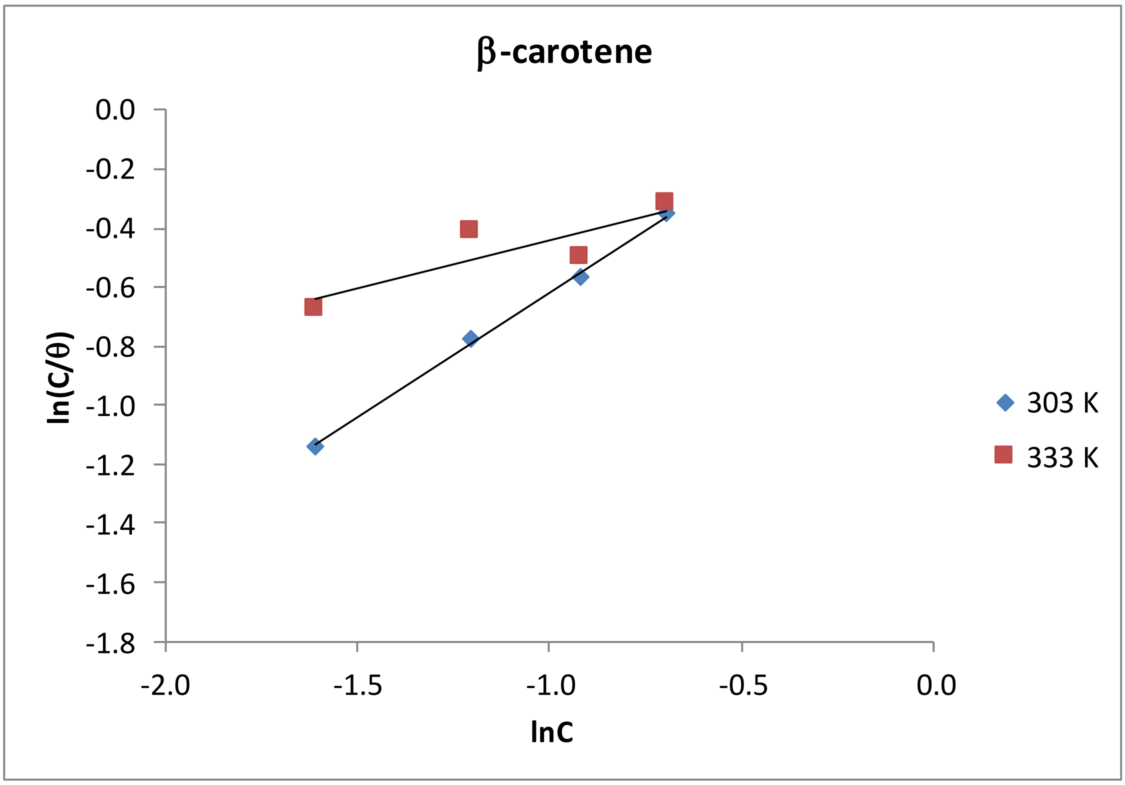


Fig. 4: Langmuir isotherm for the adsorption of β-carotene on mild steel surface

Adsorption parameters deduced from the plots are presented in Table 5. The degrees of determination (R^2) obtained for all the isotherms (except for that of β-carotene at 333K, where R^2 = 0.7320) were close to unity. However, the slopes (which ranged from 0.326 to 0.846) deviated from unity, which is expected for the ideal Langmuir isotherm. Hence there is interaction between the adsorbed species. In order to account for this interaction, other isotherms were considered and it was found that Temkin isotherm also fitted the adsorption characteristics of β-carotene.

Table 5: Langmuir and Temkin parameters for the adsorption of β-carotene on mild steel surface

Isotherm	T (K)	slope	lnK	'a'	$\Delta G^0_{ads}(kJ/mol$	R^2
Langmuir	303	0.846	0.226	-	-24.61	0.9970
Langmuir	333	0.326	0.114	-	-23.96	0.7320
Temkin	303	0.119	0.828	4.20	-28.11	0.9190
Temkin	333	0.101	0.601	4.95	-26.79	0.950

The Temkin adsorption model conceives that the degree of surface coverage varies linearly with the logarithm of the inhibitor's concentration according to the following equation (Ameh and Eddy, 2018)

$$\exp(-2\theta a) = Cb_{ads} \qquad 13$$

From the logarithm of both sides of equation 13, equation 14 is obtained, after simplification,

$$\theta = -\frac{1}{2a}\,lnC - \frac{1}{2a}lnb_{ads} \qquad 14$$

The mathematical implication of equation 14 is that a plot of θ versus lnC should be linear with slope and intercept equal to 1/2a and $-\frac{1}{2a}\,lnC$ respectively. Fig. 5 presents the Temkin plot for the adsorption of β-carotene on mild steel surface. Values of adsorption parameters calculated from the slope and intercept of the plots are also presented in Table 5. From the plots, the interaction parameters are seen to be positive. Generally positive values of 'a' indicates attraction between the adsorbed species while negative values points toward repulsion. Therefore, attraction is involved in the adsorption layer and that there is an increase in the surface energy even as the degree of surface coverage increases.

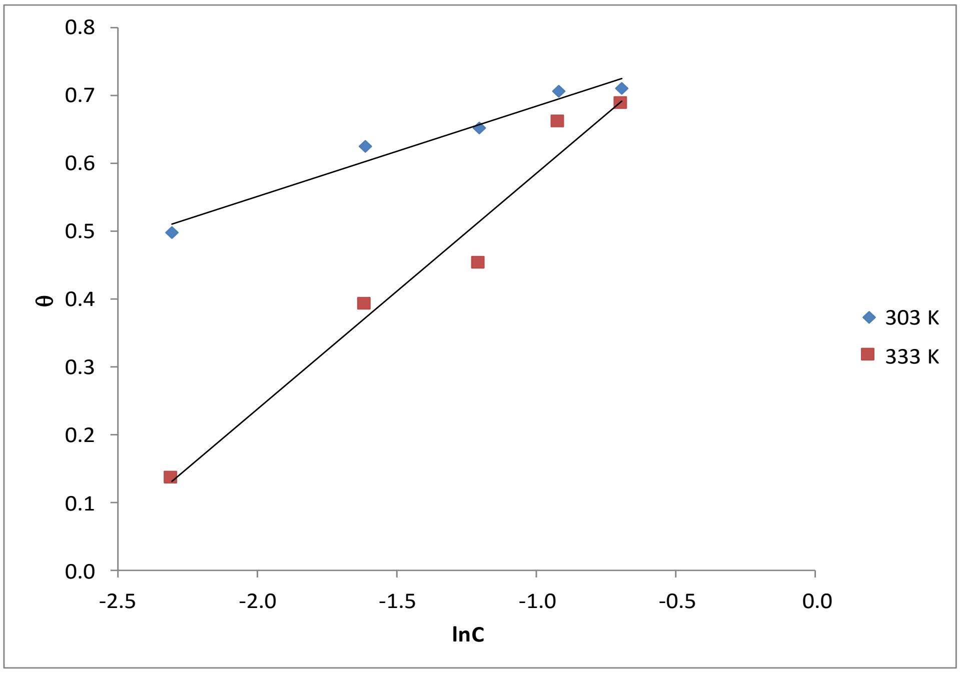


Fig. 5: Temkin isotherm for the adsorption of β-carotene on the surface of mild steel

It is significant to state that the equilibrium constant of adsorption obtained from the Langmuir and Temkin plots is related to the standard free energy of adsorption according to the following equation (Uwah *et al*., 2013d)

$$b_{ads} = \frac{1}{55.5} exp\left(\frac{\Delta G^0_{ads}}{RT}\right) \qquad 15$$

All parameters in equation 15 are as described earlier. Values of ΔG^0_{ads}obtained from equation 15 are presented in Table 12. Calculated values of ΔG^0_{ads} ranged from -23.96 to -28.71 kJ/mol. The negative values indicated that the adsorption of β-carotene on the surface of mild steel is spontaneous. These values are within the range of values expected for the mechanism of physical adsorption. Chemisorption is associated with values of ΔG^0_{ads} that are more negative than – 40 kJ/mol while ΔG^0_{ads} values upto – 20 kJ/mol are associated with physiosorption.

Quantum chemical study

Quantum chemical calculations were carried out to calculate electronic parameters for the studied inhibitors. The following semi empirical parameters were calculated: energy of the highest occupied orbital (E_{HOMO}), energy of the lowest unoccupied orbital (E_{LUMO}), energy gap, which is the difference between E_{LUMO} and E_{HOMO} (ΔE), total energy of the molecule (TE), electronic energy of the molecule (EE), dipole moment (μ) , core core repulsion energy ($_{CCRE}$) and dielectric energy (E_{dilect}). Calculations were carried out at gas and aqueous phases and the results obtained are presented in Tables 6 and 7 respectively. Fukui functions at DFT and Ab initio levels of theory and the results obtained are presented in Table 8.

Table 6: Gas phase semi empirical parameters for β-carotene at various Hamiltonians

Hamiltonian	TE (eV)	E_{elect} (eV)	E_{ccr} (eV)	μ (Debye)	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)
PM 7	-5668.19	-57596.87	51927.87	1.7112	-7.817	-0.506	7.311
PM 6	-5658.11	-57103.11	51445.00	2.2438	-7.807	-0.281	7.526
PM 3	-5600.09	-56131.89	50531.80	0.85208	-8.065	-0.757	7.308
AM1	-5888.67	-56722.73	50834.06	0.8794	-7.936	-0.591	7.345
RM1	-5803.73	-57040.35	51236.61	1.0210	-7.804	-0.226	7.578
MNDO	-5903.05	-56794.48	50891.43	0.19444	-8.160	-0.722	7.438

Table 7: Aqueous phase semi empirical parameters for β-carotene

Hamiltonian	**TE (eV)**	**$E_{dielect}$ (eV)**	**E_{elect} (eV)**	**E_{ccr} (eV)**	**μ (Debye)**	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**	**ΔE (eV)**
PM 6	-5658.51	-0.4488	-10758.74	5100.23	3.3057	-8.181	-0.624	7.557
PM 3	-5600.24	-0.1641	-9787.27	4187.03	1.1250	-8.258	-0.955	7.303
AM1	-5888.89	-0.2387	-10378.18	4489.29	1.1703	-8.145	-0.897	7.248
RM1	-5803.90	-0.18273	-10693.00	4891.85	1.4284	-8.004	-0.429	7.575
MNDO	-5903.10	-0.0448	-10449.76	4546.66	0.2044	-8.222	-0.784	7.438

Table 8: Fukui functions of β-carotene calculated from Ab initio and DFT levels of theory

	Ab initio		**DFT**	
Atom	f_k^+	f_k^-	f_k^+	f_k^-
1 6	-3.9121	0.0000	0.0000	0.0000
2 6	-3.9075	0.0000	0.0000	0.0000
3 6	-3.9014	0.0000	0.0000	0.0000
4 6	-4.0243	0.0000	0.0000	0.0000
5 6	-3.9815	0.0000	0.0000	0.0000
6 6	-4.0425	0.0000	0.0000	0.0000
7 6	-3.9357	0.0000	0.0000	0.0000
8 6	-3.9377	0.0000	0.0000	0.0000
9 6	-4.0113	0.0000	0.0000	0.0000
10 6	-3.9487	0.0000	0.0000	0.0000
11 6	-3.9439	0.0000	0.0000	0.0000
12 6	-3.9502	0.0001	0.0001	0.0003
13 6	-4.0248	0.0008	-0.0046	-0.0763
14 6	-3.9417	0.6694	2.4106	1.8408
15 6	3.6552	-0.0018	-0.0761	0.0922
16 6	4.0863	-0.0213	0.0163	0.0019
17 6	3.9304	0.0005	0.0014	0.0007
18 6	3.9614	-0.0004	0.0002	-0.0003
19 6	4.0489	0.0007	0.0008	0.0010
20 6	4.0621	0.0000	0.0002	0.0001
21 6	4.0472	-0.0001	0.0009	0.0003
22 6	4.0027	-0.0007	0.0004	-0.0032
23 6	4.0565	0.0000	0.0012	0.0689
24 6	4.0858	0.0001	0.0004	0.0009
25 6	3.9663	0.0002	0.0008	0.0004
26 6	3.9307	-0.0003	0.0001	0.0003
27 6	4.1219	0.0004	0.0030	0.0004
28 6	4.2006	-0.0763	0.1518	0.0155
29 6	4.0671	-0.0003	0.0076	0.0002
30 6	3.9923	-0.0003	-0.0007	-0.0008
31 6	4.1725	0.0029	0.0080	0.0018
32 6	4.1786	-0.1249	0.0866	-0.0453
33 6	3.9800	-0.1106	-0.1069	-0.0835
34 6	3.9106	-0.1262	-0.2120	-0.1489
35 6	4.0990	-0.1196	0.0398	-0.0061
36 6	-4.0244	0.0000	0.0000	0.0000
37 6	-3.9817	-0.0006	-0.0001	0.0017
38 6	-4.0425	0.0000	0.0000	0.0000
39 6	-3.9357	0.0000	0.0000	0.0000
40 6	-3.9377	0.0000	0.0000	0.0000

Global reactivity

The most significant parameters in the semi empirical results is the frontier molecular energies, which include the energy of the E_{HOMO}, the E_{LUMO} and the ΔE. The E_{HOMO} correlates with the electron donating ability of a specie. Higher values of E_{HOMO} is thus associated with better inhibitor. On the other hand, E_{LUMO} is associated with the tendency of a specie to accept electron. Thus, lower value of E_{LUMO} implies better inhibition efficiency. The energy gap of a molecule is associated with its softness and harness. Larger energy gap implies that the molecule will need much energy to move from HOMO to the LUMO. Therefore, larger energy gap leads to hard molecule while lower energy gap leads to soft molecule. From the results presented, it can be seen that β-carotene is has semiempirical values that are comparable to those of some good corrosion inhibitors Global softness can be calculated from the following equation (Eddy and Ita, 2011a)

$$S = \frac{1}{(E_{N-1} - E_N) - (E_N - E_{N+1})} \qquad 16$$

where E_{N-1}, E_{N+1} and E_N are the total energy of the molecule when it is in anionic, neutral and cationic forms respectively. According to Eddy *et al.* (2015), the first term in the denominator represent the electron affinity of the molecule (which is related to the E_{LUMO}) while the second term represents the ionization energy of the molecule (which is related to E_{HOMO}). Hence equation 16 can be written as follows,

$$S = \frac{1}{E_{LUMO} - E_{HOMO}} \qquad 17$$

Global hardness is the inverse of S (i.e $\eta = S^{-1}$). Calculated values of S and η for β-carotene using PM7, PM6, PM3, AM1, RM1 and MNDO are presented in Table 9. The results obtained indicated that S and η values for β-carotene are comparable to those of efficient imnhibitors (Odeoemelam *et al*., 2018)

Table 9: Gas Phase values of S and η for β-carotene at different Hamiltonians

	Aqueous phase		**Gas phase**	
Inhibitor	S	η	S	η
PM7	-	-	0.13678	7.311
PM6	0.132328	7.557	0.132873	7.526
PM3	0.13693	7.303	0.136836	7.308
AM1	0.137969	7.248	0.136147	7.345
RM1	0.132013	7.575	0.131961	7.578
MNDO	0.134445	7.438	0.134445	7.438

Other calculated semiempirical parameters were E_{TE}, E_{CCR}, E_{Elect} and μ. On the basis of quantum approach to corrosion study, a better inhibitor is expected to exhibit higher values of E_{TE}, E_{CCR} and E_{elect} as obtained in the present gas and aqueous phase data (Eddy, 2011). However, the actual relation between corrosion inhibition and μ has not been fully explored. μ is expected to be associated with the influence of charge on the inhibition efficiency. In this study, values of μ were also comparable to those of other inhibitors. This observation does not infer a perfect relationship between μ and corrosion inhibition potentials because they are reported cases, where μ values are seen to increase with corrosion inhibition efficiency (Eddy and Ita, 2011b).

Local reactivity

The local selectivity of a corrosion inhibitor is best analysed using the Fukui function. The Fukui indices permit the distinction of each part of a molecule on the basis of its chemical behaviour due to different substituent functional groups. According to Eddy and Essien (2017), the Fukui function can be formally defined as

$$f(r) = \left(\frac{\delta \sigma}{\delta v}\right)_N \qquad 18$$

where v(r) is the external potential and the functional derivatives must be taken at constant number of electrons. Assuming that the total energy E as a function of N and functional of v(r) is an exact differential, the Maxwell relations between derivatives may be applied to write as follows:

$$f(r) = \left(\frac{\delta p(r)}{\delta N}\right)_v \qquad 19$$

Equation 19 is the most standard presentation of the Fukui function. The Fukui function is provoked by the fact that if an electron δ is transferred to an N electron molecule, it will tend to distribute so as to minimize the energy of the resulting N + δ electron system. The resulting change in electron density is the nucleophilic (f^+) and electrophillic (f^-) Fukui functions which can be calculated using the finite difference approximation as follows (Eddy et al., 2010a-c)

$$f_x^+ = f(r) = \frac{\delta p(r)^+}{\delta N}_v = q_N - q_{N+1} \qquad 20$$

$$f_x^- = f(r) = \frac{\delta p(r)^+}{\delta N}_v = q_{N-1} - q_N \qquad 21$$

where ρ, $q_{(N+1)}$, $q_{(N)}$ and $q_{(N-1)}$ are the density of electron and the Milliken charge of the atom with N+1, N and N-1 electrons. Once the Fukui functions have been calculated, the sites for electrophilic and nucleophilic attacks can be accessed by assuming that they are controlled by the highest value of f^+ and f^- respectively. In this work, Fukui functions were computed for Ab initio and DFT level of theories using STO3G basic set. From the results obtained for calculated values of Fukui function using Ab initio calculations reveals that for β-carotene, the sites for electrophilic and nucleophilic attacks reside in the C(35) and C(14) atoms respectively.

CONCLUSIONS

Beta carotene is a good adsorption inhibitor for the corrosion of mild steel in acidic medium. The inhibitor is spontaneously adsorbed on the surface of mild steel and exhibited exothermic adsorption step. Quantum chemical approaches is significant to support further studies on corrosion inhibition potential of beta carotene.

Acknowledgement

The author gratefully acknowledged the academic assistant of Prof. Nnabuk Okon Eddy of the Department of Pure and Industrial Chemistry for providing the platform for the experiments and softwares for computational calculations.

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