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# Adsorption and Quantum Chemical Studies on Cloxacillin and Halides for the Corrosion of Mild Steel in Acidic Medium

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The corrosion inhibition of mild steel in $H_2SO_4$ by Cloxacillin (CLX) and its synergistic combination with halides (KI, KBr and KCl) was investigated using gravimetric, thermometric, gasometric and quantum chemical methods. The results indicated that CLX is a good adsorption inhibitor for the corrosion of mild steel in $H_2SO_4$. Inhibition efficiency of CLX on mild steel increased with increase in concentration but decreased with rise in temperature ranging from 90.40 to 93.98%, 80.85 to 86.43%, 78.41 to 84.07% and 58.61 to 77.57% at 303, 313, 323 and 333 K respectively. The combination of CLX with the halides (KCl, KBr and KI) enhanced the inhibitive and adsorption capability of CLX to a greater extent indicating synergism. The adsorption was spontaneous and the experimental data were also found to fit into the Langmuir (mean $R^2$ = 0.9978) adsorption isotherm. Physical adsorption mechanism has been proposed from the thermodynamic data obtained in the study and the activation energies of the corrosion inhibition by CLX were higher than the value obtained for the blank which signifies physical adsorption. Some quantum chemical parameters and the Mulliken charge densities on the optimized structure of CLX were calculated using the B3LYP/6-31G (d,p) basis set method to provide further insight into the mechanism of the corrosion inhibition process. The local reactivity was analyzed through the Fukui function and condensed softness indices in order to know the possible sites of nucleophillic and electrophillic attacks.

**Keywords:** corrosion inhibition, cloxacillin, halides, synergism, adsorption, adsorption isotherm, DFT -B3LYP/6-31G (d,p)., fukui functions, mulliken charges.

## 1. INTRODUCTION

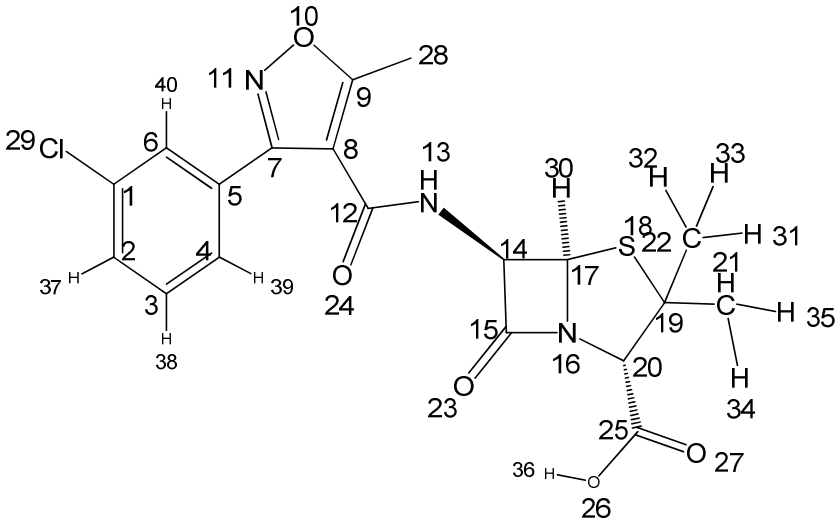
Corrosion of metals is a major industrial problem that has attracted much investigation and researches [1-6]. Corrosion is the primary means by which metals deteriorate. Most metals corrode on contact with water (and moisture in the air), acids, bases, salts, oils, aggressive metal polishes, and

other solid and liquid chemicals. The corrosion of steel in acidic solution is the most common form of corrosion and has practical importance during industrial processes such as acid pickling of iron and steel, chemical cleaning of the scale in metallurgy, oil recovery in the petroleum industries, etc [7-10]. The rate of corrosion of mild steel depends on the concentration of $H_2SO_4$, temperature, period of contact, the presence or absence of an inhibitor, etc [7-18].

An inhibitor is a substance that retards the rate of corrosion of metals when added in minute quantity [19]. Most inhibitors in use are synthesised from cheap raw materials, some are chosen from compounds having hetero atoms (N, S, O, P) in their aromatic or long carbon chain [20-22]. In our research group, we have experimented on the possibility of using some antibiotics for the inhibition of the corrosion of metals [23, 24]. A few investigations have been reported on the use of antibacterial drugs as corrosion inhibitors by some other research groups. Rhodanine azosulpha drugs have been reported as corrosion inhibitors for the corrosion of 304 stainless steel in HCl solutions using weight loss and potentiostatic polarization techniques by Abdallah [25]. They inhibited the corrosion by parallel adsorption on the surface of steel due to the presence of more than one active centre in the inhibitor. Abdallah [26] also studied some antibacterial drugs viz. ampicillin, cloxacillin, flucloxacillin and amoxicillin as corrosion inhibitors for aluminium in HCl solutions using hydrogen evolution, weight loss and potentiostat polarization techniques. The inhibitive effect of four sulpha drug compounds viz. sulfaguanidine, sulfamethazine, sulfamethoxazole and sulfadiazine on mild steel corrosion in HCl solutions was reported using both weight loss and galvanostatic polarization [27]. The sulpha drugs have a large number of functional adsorption centres (e.g. $-NH_2$ group, $-SO_2-NH-$ group, O and/or N heteroatoms and aromatic rings). They are strongly basic and are readily soluble in acidic medium. Rhodanine has also been reported as corrosion inhibitor for mild steel in HCl by Solmaz et. al. [28] using potentiodynamic polarization, electrochemical impedance spectroscopy etc. Most of the drugs used play important roles in biological reactions because of their anticonvulsant, antibacterial, antidiabetic, inhibitive to mycobacterium tuberculosis and other properties [29, 30].

Several attempts have been made to predict corrosion inhibition efficiency with a number of individual parameters obtained via various quantum chemical calculation methods as a tool for studying corrosion inhibitors [31-34]. These trials were aimed at finding possible correlations between corrosion inhibition efficiency and a number of quantum chemical properties/descriptors such as dipole moment , highest occupied ($E_{HOMO}$), lowest unoccupied ($E_{LUMO}$) molecular orbital, the difference between them (LUMO-HOMO gap), mulliken charges as well as some structural parameters. We have also recently reported on some studies using some drugs as corrosion inhibitors in our laboratories [35- 40].

Our present research is aimed at investigating the inhibitive, adsorption properties and synergistic behaviour of Cloxacillin (CLX) and halides for the corrosion of mild steel in $H_2SO_4$ using weight loss, thermometric, gasometric and some quantum chemical calculations to know the possible active centre (s) responsible for the adsorption of CLX onto the mild steel surface which will give further insight into the adsorption mechanism of the corrosion process. The chemical structure of cloxacillin, CLX {(6R) -6- [3-(2-Chlorophenyl) – 5 – methylisoxazole-4-carboxamido] penicillanic acid} with molecular formula of $C_{19}H_{18}ClN_3O_5S$ = 435.9g/mol is shown on the next page.



## 2. EXPERIMENTAL TECHNIQUES

### *2.1 Materials*

Materials used for the study were mild steel sheets of composition (wt %); Mn (0.6), P (0.36), C (0.15) and Si (0.03) and the rest Fe. The sheet was mechanically pressed cut to form different coupons, each of dimension, 5x4x0.11cm. Each coupon was degreased by washing with ethanol, dipped in acetone and allowed to dry in air before they were preserved in a desiccator. All reagents used for the study were Analar grade and double distilled water was used for their preparation.

The inhibitor, cloxacillin (CLX) was obtained locally and was used without further purification. The concentrations of the inhibitor used for the study were $2x10^{-4}$ to $12x10^{-4}$M in 1L solution of 0.1M $H_2SO_4$.

### *2.2 Gravimetric method*

In the gravimetric experiment, a previously weighed mild steel coupon was completely immersed in 250ml of the test solution in an open beaker. The beaker was inserted into a water bath maintained at 303 K. After every 24hours, each sample was withdrawn from the test solution, washed in a solution containing 50% NaOH and 100g/l of zinc dust. The washed coupons were dipped in acetone and allowed to dry in air before re-weighing. The difference in weight for a period of 168h (7 days) was taken as total weight loss. The experiments were repeated at 313, 323 and 333K respectively. From the weight loss results, the inhibition efficiency (%I) of the inhibitor, degree of surface coverage and corrosion rates were calculated using equations 1,2 and 3 respectively [38];

$$\%I = (1 - W_1/W_2) \times 100 \quad (1)$$

$$\theta = 1 - W_1/W_2 \quad (2)$$

$$CR\ (gh^{-1}cm^{-2}) = W/At \quad (3)$$

where $W_1$ and $W_2$ are the weight losses (g) for mild steel in the presence and absence of the inhibitor in $H_2SO_4$ solution, θ is the degree of surface coverage of the inhibitor, A is the area of the mild steel coupon (in $cm^2$), t is the period of immersion (in hours) and W is the weight loss of mild steel after time, t. All the measurements were performed in triplicate and the mean value recorded.

*2.3 Gasometric method*

The gasometric experiment was carried out at 303 K as described in literature [17]. From the volume of hydrogen evolved per minute, inhibition efficiencies were calculated using equations 4 below.

$$\%I = \left(1 - \frac{V_{Ht}^{1}}{V_{Ht}^{o}}\right) x\,100 \qquad (4)$$

where $V_{Ht}^{1}$ and $V_{Ht}^{o}$ are the volumes of $H_2$ gas evolved at time‘t’ for inhibited and uninhibited solutions respectively.

*2.4 Thermometric method*

This was also carried out as reported elsewhere [17]**.** From the rise in temperature of the system per minute, the reaction number (RN) was calculated using equation 5:

$$RN\left(^{o}C\ \min^{-1}\right) = \frac{T_m - T_i}{t} \qquad (5)$$

where $T_m$ and $T_i$ are the maximum and initial temperatures respectively and ‘t’ is the time (min) taken to reach the maximum temperature. The inhibition efficiency (%I) of the inhibitor was evaluated from percentage reduction in the reaction number namely.

$$\%I = \frac{RN_{aq} - RN_{wi}}{RN_{aq}} x100 \qquad (6)$$

where $RN_{aq}$ is the reaction number in the absence of inhibitors (blank solution) and $RN_{wi}$ is the reaction number of the $H_2SO_4$ containing studied inhibitors.

*2.5 Quantum chemical calculations*

The molecular sketch of cloxacillin (CLX) was drawn using the Gauss View 3.0. All the quantum calculations were performed with complete geometry optimization by using standard

Gaussian03 (Review B.05) software package [41]. The quantum chemical parameters were calculated using the density functional theory (DFT) method at the level of B3LYP/ 6-31G (d,p). The following quantum chemical parameters were considered: the energy of the highest occupied molecular orbital ($E_{HOMO}$), the energy of the lowest unoccupied molecular orbital ($E_{LUMO}$), the dipole moment ($\mu$) , total negative charge (*TNC*) on the molecule, intrinsic molecular volume (*Vi*) and dipolar-polarizability factor ($\pi$*). The Mulliken and Lowdin charges as well as the Fukui indices were computed using the Games software.

## 3. RESULTS AND DISCUSSION

### *3.1 Effect of cloxacillin on the corrosion of mild steel*

Figs. 1 shows the variation of weight loss with time for the corrosion of mild steel in 0.1 M $H_2SO_4$ containing various concentrations of CLX at 303 K (plots for other temperatures are not shown).

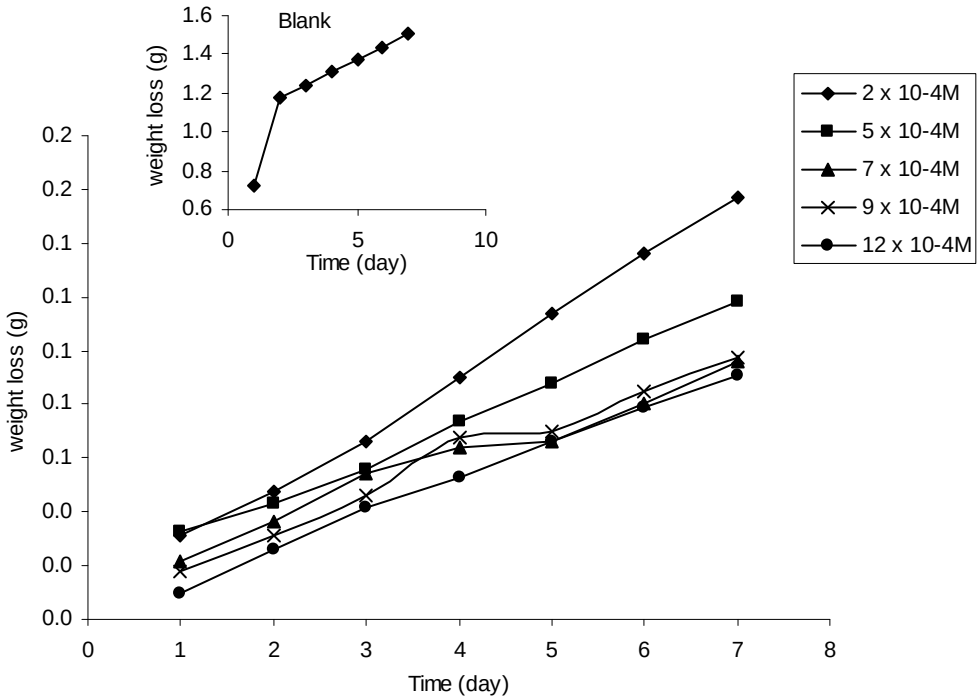



**Figure 1.** Variation of weight loss with time for the corrosion of mild steel in 0.1 M $H_2SO_4$ containing various concentrations of CLX (insert is the plot for the blank).

From the Figures, it is apparent that weight loss of mild steel increases with the period of contact and temperature but decreases as the concentration of CLX is increased indicating that the rate of corrosion of mild steel increased with increase in the period of contact and temperature. The results

also indicate that CLX inhibited the corrosion of mild steel in $H_2SO_4$. The values of the corrosion rates of mild steel in various media are presented in Table 1. The results revealed that the corrosion rates of mild steel in the presence of the inhibitor were lower than the corresponding values obtained for the blank indicating that CLX retarded the rate of corrosion of mild steel in $H_2SO_4$. The values of % inhibition efficiency of CLX obtained from weight loss measurements are also presented in Table 1.

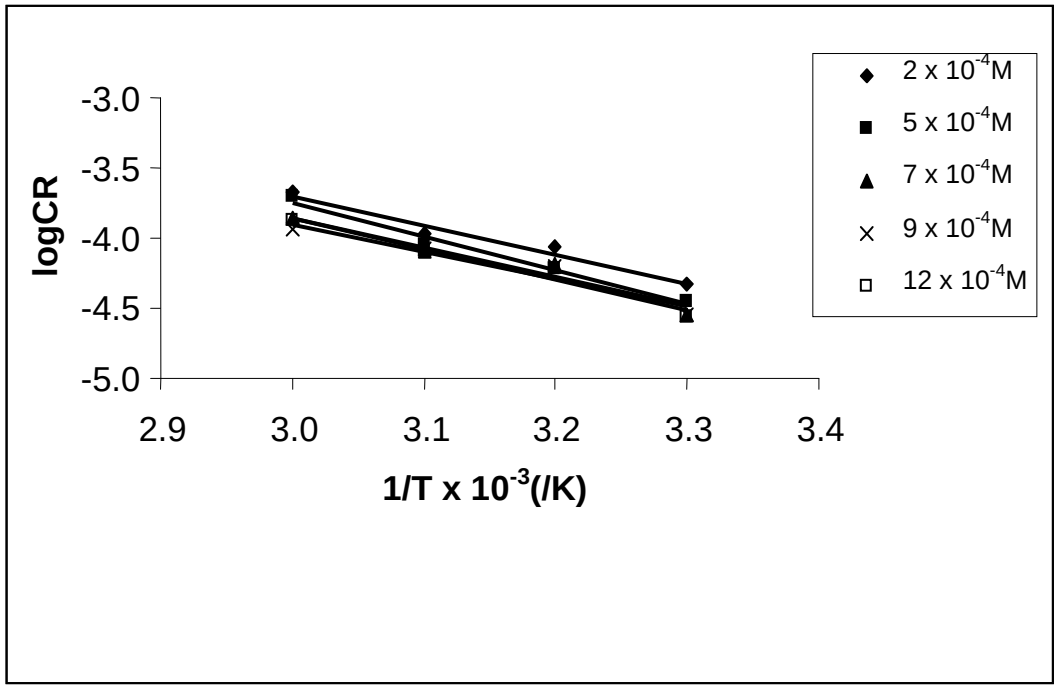



**Figure 2.** Plots of log CR versus 1/T for the corrosion of mild steel in $H_2SO_4$ containing various concentrations of CLX

The results indicate that the inhibition efficiency of CLX increased with increase in its concentration but decreased with increase in temperature indicating that CLX is an adsorption inhibitor for mild steel corrosion and that the mechanism of adsorption of the inhibitor is through physical adsorption [7-10, 26]. From the variation of volume of hydrogen gas evolved with time (plots not shown) during the corrosion of mild steel in various concentrations of $H_2SO_4$. it was seen that the volume of hydrogen gas evolved decreases as the concentration of CLX is increased. This also indicates that the rate of corrosion of mild steel in $H_2SO_4$ is inhibited by various concentrations of CLX. The values of inhibition efficiencies of CLX calculated from gasometric and thermometric methods are also presented in Table 1. The inhibition efficiencies obtained from weight loss measurements were close to those obtained from gasometric and thermometric methods indicating that the methods are comparable [42].The inhibition efficiencies calculated from thermometric and gasometric methods correlated strongly with those obtained from gravimetric method (at 303K) ($R^2$ = 0.9328 and 0.9317 for thermometric and gasometric data respectively).

*3.2 Effect of temperature*

The effect of temperature on the corrosion of mild steel in $H_2SO_4$ containing various concentrations of CLX was investigated using the Arrhenius equation below;

$$\log CR = \log A - E_a/2.303RT \quad (7)$$

Plots of logCR versus 1/T yielded straight lines with $R^2$ values tending to unity. The linearity of the plots (Fig. 2) indicates that the corrosion of mild steel in the presence of CLX is consistent with Arrhenius theory. Values of $E_a$ calculated from the slopes of the Arrhenius plot are recorded in Table 2. These values ranged from 36.93 to 46.05 kJ/mol. The results obtained are consistent with the mechanism of physical adsorption because values of $E_a$ are lower than threshold value of 80 kJ/mol [43 - 45].

**Table 1**. Corrosion rates of mild steel and inhibition efficiency of CLX for mild steel corrosion.

| **Conc. (M)** | **Inhibition efficiency (%I) Gravimetric method** | | | | **Corrosion rates ($gh^{-1}cm^{-2}$) x $10^{-4}$** | | | | **Inhibition efficiency (%I) Thermometric** | **Gasometric** |
|---|---|---|---|---|---|---|---|---|---|---|
| | **303 K** | **313 K** | **323 K** | **333 K** | **303 K** | **313 K** | **323 K** | **333 K** | **303 K** | **303 K** |
| **2 x $10^{-4}$** | 90.40 | 78.41 | 80.85 | 58.61 | 0.05 | 0.09 | 0.11 | 0.21 | 85.70 | 71.00 |
| **5 x $10^{-4}$** | 92.80 | 82.02 | 85.24 | 62.13 | 0.04 | 0.06 | 0.09 | 0.20 | 88.00 | 79.07 |
| **7 x $10^{-4}$** | 92.80 | 83.45 | 85.97 | 73.61 | 0.03 | 0.07 | 0.08 | 0.14 | 90.00 | 82.24 |
| **9 x $10^{-4}$** | 92.80 | 83.72 | 86.29 | 74.19 | 0.03 | 0.06 | 0.08 | 0.12 | 92.80 | 86.03 |
| **12 x $10^{-4}$** | 93.98 | 84.07 | 86.43 | 77.57 | 0.03 | 0.36 | 0.08 | 0.13 | 92.80 | 88.39 |

*3.3 Thermodynamic and adsorption considerations*

In order to calculate thermodynamic parameters for the adsorption of CLX on mild steel surface ($\Delta H_{ads}$ and $\Delta S_{ads}$), the transition state equation below was used [13,19]:

$$CR = RT/Nh(\exp(\Delta S_{ads}/R)\exp(-\Delta H_{ads}/RT) \quad (8)$$

where N is Avogadro's number, h is the Planck constant. From the logarithm of both sides of equation 8, equation 9 was obtained:

$$\log(CR/T) = \log(R/Nh) + \Delta S_{ads}/2.303R - \Delta H_{ads}/2.303RT \quad (9)$$

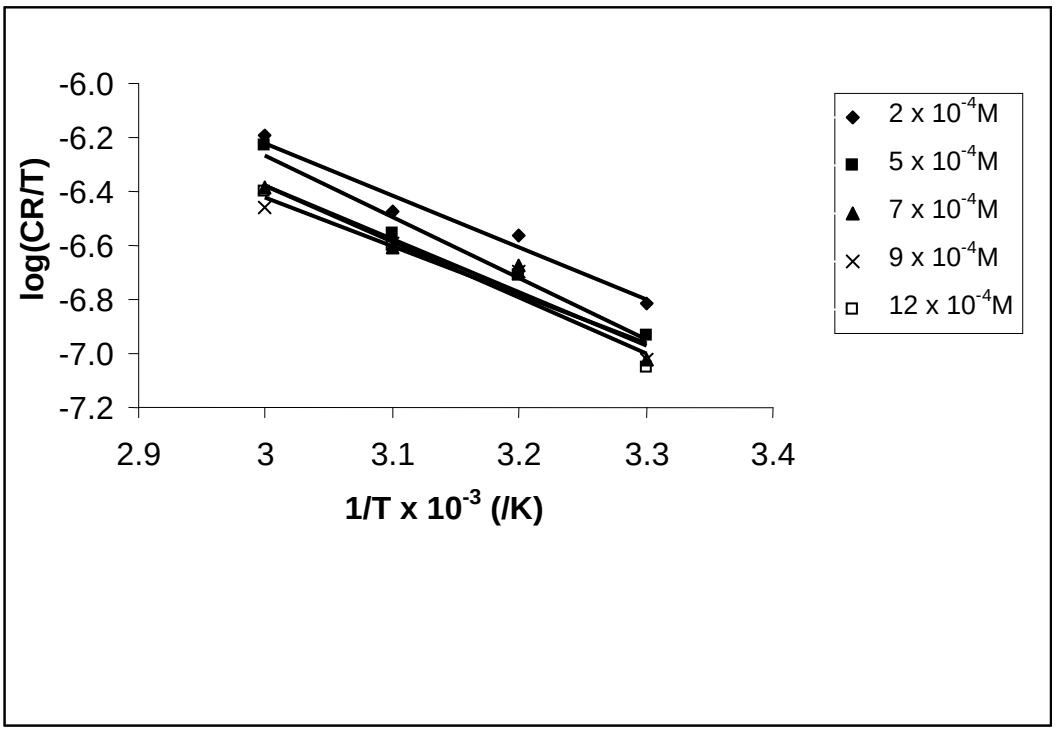



**Figure 3.** Plots of log (CR/T) versus 1/T for the corrosion of mild steel in 0.1 M $H_2SO_4$ containing various concentrations of CLX.

Plots of log(CR/T) versus 1/T from data obtained from the weight loss measurements gave straight lines (Fig.3) and the slope and intercept of the plots are respectively equal to $\Delta H_{ads}/2.303R$ and $(\log(R/Nh) + \Delta S_{ads}/2.303R)$. From the results obtained, values of $\Delta H_{ads}$ ranged from 34.31 to 43.43 kJ/mol (mean = 38.54 kJ/mol) indicating that the corrosion of mild steel in the presence of CLX is endothermic. $\Delta S_{ads}$ values ranged from -204.71 to -217.66J/mol (mean = -217.6647J/mol).

Adsorption isotherms have been used to explain the mode of adsorption of CLX on mild steel surface. The degree of surface coverage ($\theta$) for the different concentrations of the inhibitors at different temperatures evaluated from weight loss measurements was used to fit curves for the different adsorption isotherms.

The adsorption of CLX on the surface of mild steel was found to follow the Langmuir isotherm. The degree of surface coverage of CLX relates to its concentration, C according to equation 10 [4,20]

$$\theta = kC \times 1/(1+KC) \qquad (10)$$

where K designates the adsorption equilibrium constant. From the rearrangement of equation 10, equation 11 is obtained which can also be expressed as equation 12,

$$1/K + C = C/\theta \qquad (11)$$

$$\log(C/\theta) = \log C - \log K \quad (12)$$

From equation 12, a plot of log(C/θ) versus logC produced straight lines with intercept logK Fig. 4 shows Langmuir isotherm for the adsorption of CLX on mild steel surface. Values of Langmuir adsorption parameters are recorded in Table 3.

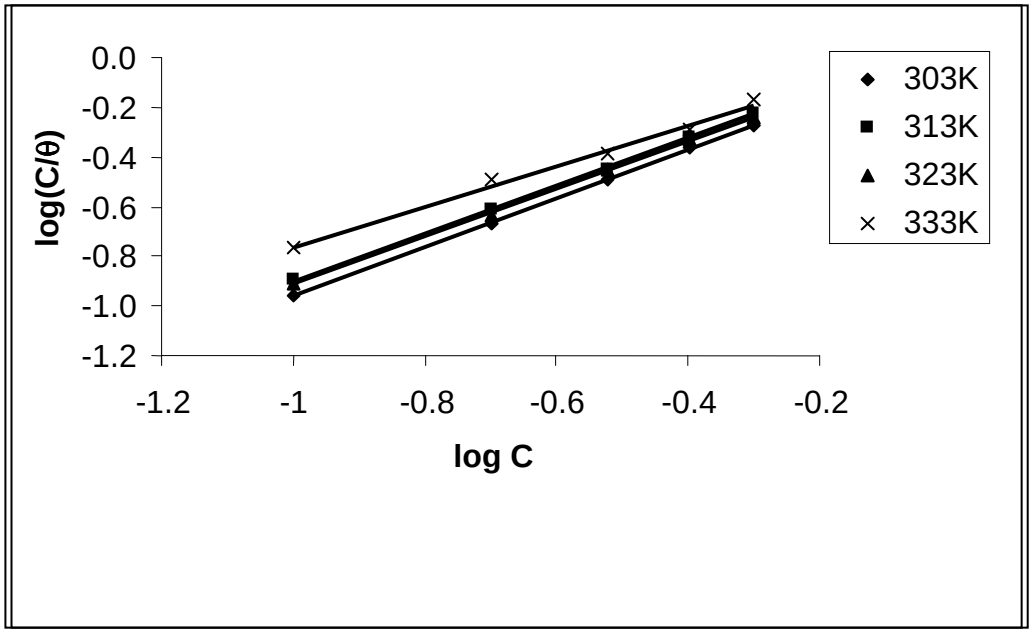



**Figure 4.** Langmuir adsorption isotherm for the adsorption of CLX on the surface of mild steel

**Table 2**. Some thermodynamic parameters for the adsorption of CLX on mild steel surface.

| Conc. (M) | $E_a$ (kJ/mol) | $R^2$ | $\Delta H_{ads}$ (kJ/mol) | $\Delta S_{ads}$ (J/mol) | $R^{2*}$ |
|---|---|---|---|---|---|
| **2 x $10^{-4}$** | 36.93 | 0.9711 | 37.33 | -204.79 | 0.9670 |
| **5 x $10^{-4}$** | 39.92 | 0.9824 | 43.43 | -207.90 | 0.9801 |
| **7 x $10^{-4}$** | 40.51 | 0.9493 | 37.89 | -206.03 | 0.9371 |
| **9 x $10^{-4}$** | 42.35 | 0.9400 | 34.31 | -217.66 | 0.9316 |
| **12 x $10^{-4}$** | 46.05 | 0.9630 | 39.74 | -200.52 | 0.9585 |
| **Mean** | **41.15** | | **38.54** | **-207.38** | |

$R^2$ = degree of linearity for the plot of log CR versus 1/T,
$R^{2*}$ = degree of linearity for the plot of log (CR/T) versus 1/T,
$\Delta H_{ads}$ = enthalpy of adsorption,
$\Delta S_{ads}$ = entropy of adsorption

**Table 3**. Langmuir adsorption parameters for the adsorption of CLX on mild steel surface.

| | Temperature (K) | log K | Slope | $\Delta G_{ads}$ (kJ/mol) | $R^2$ |
|---|---|---|---|---|---|
| **Langmuir** | 303 | 0.0216 | 0.9794 | -10.25 | 0.9999 |
| | 313 | 0.0602 | 0.9583 | -10.47 | 0.9997 |
| | 323 | 0.0492 | 0.9628 | -10.40 | 0.9994 |
| | 333 | 0.0573 | 0.9801 | -10.45 | 0.9923 |

**K = equilibrium constant of adsorption,
$\Delta G_{ads}$ = free energy of adsorption,
$R^2$ = degree of linearity

**Table 4.** Inhibition efficiencies of various concentrations of CLX in combination with 0.06 M halides and synergistic parameters

| Conc. | %I (303 K) | | | %I (333 K) | | | $S_I$ (303 K) | | | $S_I$(333 K) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (M) | KBr | KI | KCl | KBr | KI | KCl | KBr | KI | KCl | KBr | KI | KCl |
| **$2 \times 10^{-4}$** | 93.12 | 87.63 | 97.29 | 85.27 | 64.23 | 85.45 | 1.94 | 0.55 | 9.65 | 6.85 | 1.20 | 8.60 |
| **$5 \times 10^{-4}$** | 94.23 | 89.58 | 97.69 | 87.66 | 65.36 | 86.24 | 1.43 | 0.76 | 4.75 | 8.09 | 1.41 | 7.21 |
| **$7 \times 10^{-4}$** | 95.06 | 91.33 | 97.92 | 89.47 | 66.95 | 86.24 | 1.13 | 0.54 | 5.77 | 8.56 | 0.84 | 6.43 |
| **$9 \times 10^{-4}$** | 95.37 | 94.46 | 97.90 | 89.59 | 67.57 | 86.34 | 1.00 | 1.00 | 7.00 | 8.29 | 0.80 | 5.70 |
| **$12 \times 10^{-4}$** | 95.52 | 94.48 | 98.35 | 89.75 | 68.86 | 87.87 | 0.64 | 2.41 | 4.53 | 8.77 | 0.94 | 6.33 |

Based on the linearity of the plots (indicated by the respective values of $R^2$) and the closeness of the slopes to unity, it can be inferred that Langmuir adsorption isotherm is obeyed.

Values of free energy of adsorption of CLX on mild steel surface were calculated using equation 13[46-49]

$$\Delta G_{ads} = -RT \ln (55.5K) \quad (13)$$

where K is the equilibrium constant of adsorption, R is the molar gas constant and T is the temperature. Using values of K obtained from Langmuir adsorption isotherm. $\Delta G_{ads}$ values were obtained (see Table 3) and were found to be negative and less than the threshold value (-40 kJ/mol) indicating that the adsorption of CLX on the surface of mild steel is spontaneous and followed the mechanism of physical adsorption[43-45,50-53].

**Table 5.** Adsorption parameters for joint adsorption of halides and CLX

| **Parameters** | **0.06M KBr + CLX** | **0.06MKI + CLX** | **0.06MKCl + CLX** |
|---|---|---|---|
| **$\Delta G_{ads}$(303K)** | -4.06 | -0.53 | -9.60 |
| **$\Delta G_{ads}$(333K)** | -16.31 | -14.84 | -16.25 |
| **$Q_{ads}$(kJ/mol)** | -23.83 | -48.58 | -35.05 |
| **$\Delta S_{ads}$(J/mol)** | 112.29 | 185.70 | -403.09 |
| **$E_a$(kJ/mol)** | 18.06 | 7.44 | 17.23 |

*3.4 Synergistic study*

Synergistic study was carried out by combining fixed concentration (0.06 M) of KCl, KBr and KI with the inhibitor (cloxacillin) using weight loss method at 303 and 333 K. Synergistic parameter ($S_I$) was calculated for each set of halide-inhibitor mixture using the following equation [54-58];

$$S_1 = \frac{1 - I_{1+2}}{1 - I'_{1+2}} \qquad (14)$$

where $I_{1+2} = I_1 + I_2$: $I_1$ is the inhibition efficiency of the halide, $I_2$ is the inhibition efficiency of the inhibitor (cloxacillin), $I'_{1+2}$ is the inhibition efficiency of the inhibitor in combination with 0.06 M halide (KI, KBr or KCl). Table 5 shows the values of $S_I$ calculated from weight loss measurements.

At, 303K, a combination of different concentrations of CLX with 0.06M KBr and 0.06MKCl respectively led to enhanced inhibition efficiency. $S_I$ values were greater than unity in all cases, indicating that the enhancement of inhibition efficiency is due to synergism. When CLX was combined with KI, synergism was observed at CLX concentrations of 9 x $10^{-4}$ and 12 x $10^{-4}$M but at concentrations of 2 x $10^{-4}$ - 7 x $10^{-4}$M, values of $S_I$ were less than unity indicating that the adsorption of CLX shows antagonistic effect on the adsorption of KI. At 333K, synergism was observed for all combinations of CLX with 0.06MKBr and 0.06MKCl respectively indicating that the enhancement in inhibition efficiency of CLX at this temperature may be due to synergism. However, when different concentrations of CLX were added to 0.06MKI, synergism was observed at concentrations of 2 x $10^{-4}$ and 5 x $10^{-4}$M but at other concentrations, antagonism was observed ($S_I < 1$).

At 303K and 333K, adsorption of CLX on mild steel surface was found to occur according to Langmuir adsorption isotherm. This implies that the concentration of the inhibitor ($C_{inh}$) is related to its degree of surface coverage according to equation 12. Values of the binding constant (K) calculated from intercepts of the Langmuir adsorption plots were used to calculate the free energies of adsorption of CLX on mild steel surface using equation 13. Calculated values of $\Delta G_{ads}$ at 303 - 333K shown in

Table 5 were found to be negative and less than -40 kJ/mol indicating that the adsorption of CLX on mild steel surface is spontaneous and proceeded via physical adsorption mechanism.

In order to calculate the heat of adsorption ($Q_{ads}$) for the combination of inhibitor (cloxacillin) with halides (KCl, KBr and KI), equation 15 was used [7-11, 20]:

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] x \left(\frac{T_{1X}T_2}{T_2 - T_1}\right) kJmol^{-1} \quad (15)$$

where $\theta_2$ and $\theta_1$ are degrees of surface coverage at temperatures of 333K ($T_2$) and 303K($T_1$) respectively and R is the molar gas constant.

These values are also presented in Table 5. The values are negative for all combinations of inhibitor with 0.06M KCl, KBr and KI indicating that the adsorption of the inhibitor-KCl, KBr and KI is spontaneous

In order to calculate the activation energy for the corrosion of mild steel in the presence of the combination of inhibitor (cloxacillin) and halides (KI, KBr and KCl), the logarithmic form of the Arrhenius equation (equation 16) was used:

$$\log\frac{CR_2}{CR_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (16)$$

where $CR_1$ and $CR_2$ are the corrosion rates of mild steel at the temperatures, $T_1$(303 K) and $T_2$ (333K) respectively.

The activation energies calculated from equation 17 (see Table 5) are positive and lesser than values obtained for inhibition of corrosion by the inhibitor alone (see Table 2) when they are not combined with halides indicating that there is an increased stability due to halides - inhibitors combination.

Values of entropy of adsorption ($\Delta S_{ads}$) for combinations of CLX with halides (KI, KBr and KCl) were calculated using Gibbs equation:

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \quad (17)$$

Calculated values of $\Delta S_{ads}$ are recorded in Table 6. These values are positive for all combinations of 0.06KBr and 0.06KI with cloxacillin, but negative for combination of 0.06MKCl with CLX.

**Table 6.** Quantum chemical parameters of cloxacillin using gas phase B3LYP/6-31G (d,p)

| Quantum parameters | Cloxacillin |
|---|---|
| $V_i$ ($cm^3$/M) | 197.52 |
| π* | 4.57 |
| $E_{HOMO}$ (eV) | -0.2422 |
| $E_{LUMO}$ (eV) | -0.0492 |
| $E_{L-H}$ (eV) | 0.193 |
| μ(Debye) | 2.7218 |
| TNC | -3.286 |

*3.6 Quantum chemical studies*

The effectiveness of an inhibitor can be related to its spatial molecular structure, as well as with their molecular electronic structure [59]. Inhibitor efficiency depends on the structure and the chemical properties of the inhibitor being adsorbed.

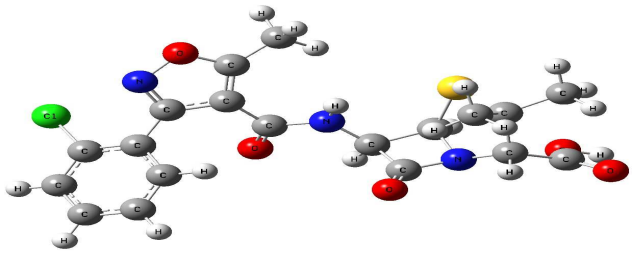


**Figure 5.** Optimized Structure of Cloxacillin (CLX).

The inhibitor layer has been related to the electronic structure of the molecule [21]. The charge and orientation of the inhibitor molecule at the metal surface are also important. Molecular modelling and frontier orbital theory has been proven to help in predicting the adsorption centre of the inhibitor molecule responsible for principal interaction. For example, an aromatic ring in the molecule with N

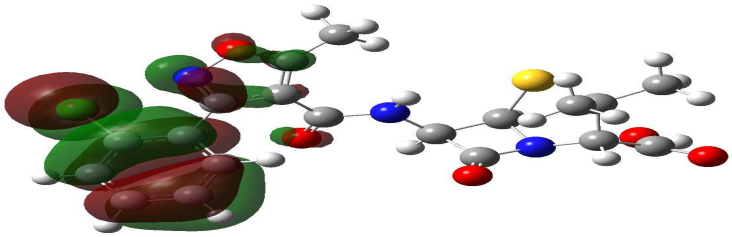


**Figure 6**. HOMO of Cloxacillin (CLX) using B3LYP/6-31G (d,p).

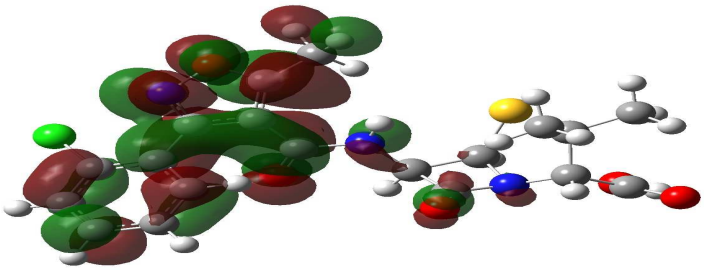


**Figure 7.** LUMO of Cloxacillin (CLX) using B3LYP/6-31G (d,p).

and O atoms are almost always favourable for effective adsorption. Also, there are certain quantum chemical parameters that can be related to the metal-inhibitor interaction namely $E_{HOMO}$, $E_{LUMO}$, $\Delta E=E_{LUMO} - E_{HOMO}$, dipole moment, $\mu$ etc. The $E_{HOMO}$ is often associated with the capacity of a molecule to donate electrons and an increase in the value of the $E_{HOMO}$ can facilitate the adsorption and therefore the inhibition efficiency by indicating the disposition of the molecule to donate orbital electrons to an appropriate acceptor with empty molecular orbital. In the same way, low values of the energy gap, $\Delta E=E_{LUMO} - E_{HOMO}$ will render good inhibition efficiencies, because the energy needed to remove an electron from the last occupied orbital will be low. Similarly, low values of the dipole moment, $\mu$ will favour the accumulation of inhibitor molecules on the metallic surface [60]. The optimized structure of CLX is shown in Fig. 5 and the HOMO and LUMO diagrams of CLX are shown in Figs. 6 and 7. Figs. 6 and 7 shows that the most susceptible sites for electrophillic attack may

occur at the nitrogen, oxygen atoms and probably the chlorine atom attached to the phenyl ring. Fig. 8 shows the Mulliken charge densities calculated on the optimized geometry of CLX using the B3LYP/6-31G (d,p) method. The results of some of the quantum chemical parameters calculated using the DFT method - B3LYP/6-31G (d,p) basis set are presented in Table 6.

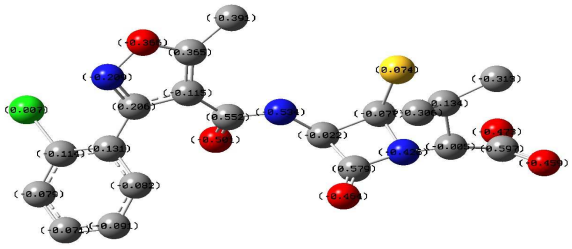


**Figure 8.** Mulliken charges on the optimized structure of Cloxacillin (CLX) using B3LYP/6-31G (d,p).

The results seem to indicate that both the values of the energy gap, $\Delta E=E_{LUMO} - E_{HOMO}$ as well as that of the dipole moment, $\mu$ favour CLX implying its effectiveness as a corrosion inhibitor. The negative sign of the $E_{HOMO}$ value obtained and other thermodynamic parameters indicates that the data obtained supports physical adsorption mechanism. Also from the molecular orbital density distribution of CLX, it is observed that the electron densities of the frontier orbitals are well proportioned. This type of structure is difficult to form chemical bond active centres which supports that the mechanism is by physical adsorption by π-stacking between the interaction sites.

Similar results were obtained for the sulphonamides [42]. The use of Mulliken population analyses to probe adsorption centres of inhibitors have been widely reported [61 - 64]. There is a general consensus by several authors that the more negatively charged an heteroatom is the more it can be adsorbed on the metal surface through the donor-acceptor type reaction [65 - 67]. It has also been reported that electrophiles attack molecules at sites of negative charge [68], which means that from the values of Mulliken charges in Fig. 8, it is possible to observe that all the nitrogen atoms present a considerable excess of negative charge -0.289,-0.534 and -0.426 and negative charges around most carbon atoms of the aromatic rings. Similar observation can be made for the oxygen atoms (-0.355, -0.501, -0.464, -0.473 and -0.459).

The local selectivity of an inhibitor was analysed using condensed Fukui and condensed softness functions. The condensed Fukui function and condensed softness are indices which allow for

the distinction of each part of a molecule on the basis of its chemical behaviour due to different substituent functional groups. The Fukui function is motivated 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 nucleophillic ($f^+$) and electrophillic ($f^-$) Fukui functions and can be calculated using the finite difference approximation as follows,

$$f_x^+ = (\delta\rho(r)/\delta N)^+_\upsilon = q_{(N+1)} - q_{(N)} \quad (18)$$

$$f_x^- = (\delta\rho(r)/\delta N)^-_\upsilon = q_{(N)} - q_{(N-1)} \quad (19)$$

where ρ, $q_{(N+1)}$, $q_{(N)}$ and $q_{(N-1)}$ are the density of electron, the Mulliken (Lowdin) charge of the atom with N+1, N and N-1 electrons. Calculated values of $f_x^+$ and $f_x^-$ (calculated from Mulliken and Lowdin charges) for the carbon and other electronegative elements are presented in Table 7.

From the results obtained, it is expected that the site for nucleophillic attack is the place where the value of $f_x^+$ is maximum while the site for electrophillic attack is controlled by the value of $f_x^-$. Therefore, the site for nucleophillic attack is at the phenyl carbon atom (C 4) while the site for electrophillic attack is in the C-Cl bond (Cl 29).

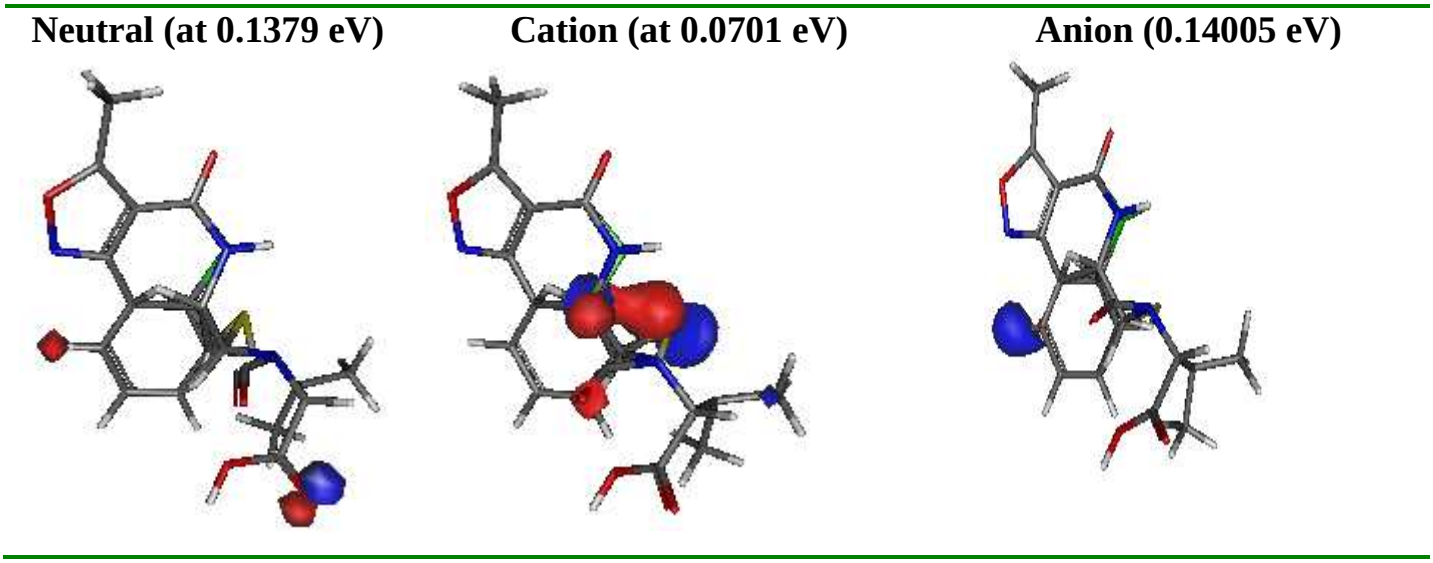



**Figure 9.** Electron density diagrams of neutral, cationic and anionic forms of CLX

The local softness, S for an atom is the product of the condensed Fukui function (f) and the global softness (S) and can be calculated using the following equations

$$S_x^+ = (f^+)S \quad (20)$$

$$S_x^- = (f^-)S \quad (21)$$

The local softness contains information similar to those in the condensed Fukui function plus additional information about the total molecular softness, which is related to the global reactivity with respect to a reaction partner.

**Table 7.** Fukui and global softness indices for nucleophillic and electrophillic attacks on CLX (calculated from Mulliken (Lowdin) charges

| | **f+** | **f-** | **S+** | **S-** |
|---|---|---|---|---|
| 1 C | 0.204(0.056) | -7.171(-6.998) | 1.195(0.329) | -42.044(-41.031) |
| 2 C | 0.006(0.003) | -7.991(-8.014) | 0.036(0.016) | -46.855(-46.988) |
| 3 C | -0.437(0.171) | -8.155(-7.755) | -2.564(1.003) | -47.811(-45.466) |
| 4 C | **8.588(7.357)** | -3.130(-2.532) | **50.350(43.136)** | -18.349(-14.844) |
| 5 C | 3.916(4.156) | 4.466(3.550) | 22.958(24.365) | 26.187(20.812) |
| 6 C | 6.544(5.309) | -6.816(-5.195) | 38.367(31.128) | -39.964(-30.458) |
| 7 C | -0.036(0.026) | 8.033(7.972) | -0.211(0.153) | 47.097(46.738) |
| 8 C | 0.000(0.000) | 7.996(7.999) | 0.000(-0.001) | 46.879(46.899) |
| 9 C | 0.001(0.000) | 7.998(8.000) | 0.009(0.001) | 46.895(46.906) |
| 10 O | 0.000(0.000) | 8.000(7.999) | 0.002(0.000) | 46.905(46.901) |
| 11 N | 0.000(0.000) | 8.002(7.999) | 0.001(0.001) | 46.915(46.896) |
| 12 C | -0.018(-0.021) | 7.994(7.999) | -0.104(-0.124) | 46.868(46.901) |
| 13 N | -0.139(-1.021) | 7.469(7.495) | -0.817(-5.983) | 43.793(43.945) |
| 14 O | 0.001(0.000) | 8.000(7.998) | 0.008(-0.001) | 46.903(46.893) |
| 15 C | 4.077(4.049) | -3.452(-3.396) | 23.906(23.740) | -20.239(19.913) |
| 16 C | -0.534(-0.586) | -7.349(-7.076) | -3.131(-3.438) | -43.088(-41.488) |
| 17 N | -0.004(0.005) | -8.007(-7.985) | -0.023(-0.030) | -46.944(-46.814) |
| 18 C | -0.247(-0.003) | -6.906(-6.974) | -1.447(-0.019) | -40.488(-40.891) |
| 19 S | 0.020(-0.002) | -3.803(-3.818) | 0.115(-0.012) | -22.295(-22.383) |
| 20 C | 0.073(-0.049) | -8.127(-7.921) | 0.427(-0.287) | -47.650(-46.439) |
| 21 C | -0.001(-0.003) | -8.358(-7.792) | -0.003(-0.018) | -49.005(-45.683) |
| 22 C | -6.474(-6.445) | 2.837(2.953) | -37.960(-37.785) | 16.633(17.315) |
| 23 C | 0.001(0.000) | -8.003(-7.998) | 0.007(-0.003) | -46.920(-46.893) |
| 24 O | -1.565(-1.483) | -0.498(-0.722) | -9.178(-8.694) | -2.923(-4.233) |
| 25 C | -0.117(-0.261) | -1.651(-1.801) | -0.684(-1.533) | -9.682(-10.560) |
| 26 O | -2.361(-2.214) | 2.359(2.186) | -13.845(-12.979) | 13.830(12.815) |
| 27 O | 0.000(-0.001) | -5.859(-5.755) | 0.002(-0.006) | -34.354(-33.742) |
| 28 C | 0.000(0.000) | 7.991(8.001) | 0.003(0.000) | 46.853(46.912) |
| 29 Cl | -4.014(-2.674) | **9.076(8.098)** | -23.531(-15.677) | **53.213(47.477)** |

The relative nucleophillicity and electrophillicity are defined as ($S^+/S^-$) and ($S^-/S^+$), respectively. The local softness indices for cloxacillin are also presented in Table 7. The results obtained are in agreement with those obtained from condensed Fukui functions. Fig. 9 shows the electron density diagram of neutral, anionic and cationic forms of Cloxacillin (red represent positive while blue represent negative). The figures support the findings made through Fukui and global softness indices. It should also be pointed out that the anion corresponds to the HOMO while the cation corresponds to the LUMO hence from the figures; it is also true that the sites for nucleophillic and electrophillic attacks are in the phenyl carbon and in the C-Cl bond respectively.

## 4. CONCLUSIONS

From the results of the study, cloxacillin is a good adsorption inhibitor for the corrosion of mild steel in $H_2SO_4$. The inhibition efficiency of cloxacillin was further enhanced by synergistic combination with halides. The adsorption of cloxacillin on mild steel surface and in combination with halides is spontaneous and obeys the mechanism of physical adsorption from the calculated thermodynamic data. The experimental data obtained in the study fitted the Langmuir adsorption isotherm (mean $R^2$ = 0.9978) best. Quantum chemical calculations using the B3LYP/6-31G (d,p) revealed that the sites for nucleophillic and electrophillic attacks are on the phenyl carbon (C4) and the C-Cl bond (C29) respectively.

## References

1. S. T. Arab, A. M. Al-Turkustani, *Portugaliae Electrochimica Acta* 24(2006) 53.
2. S. S. Mahmoud, M. Ahmed, *Portugaliae Electrochimica Acta* 24(2006) 37.
3. W. A. Monika, A. D. Siddique, *Portugaliae Electrochimica Acta* 23(2005) 445.
4. Chetounani, B.B. Hammouti, M. Benkaddour,*Pigment & Resin Tech* 33(2004) 26.
5. N. O. Eddy, E.E. Ebenso , *Pigment & Resin Tech* 39(2010) 77.
6. S. A. Abd El-Rehim, M.A.M. Ibrahim, K.F. Khaled *J. Appl. Electrochem.* 29(1999) 593.
7. I.B. Obot, N. O. Obi-Egbedi, S.A. Umoren, *Int. J. Electrochem. Sci.* 4(2009) 863.
8. S. Vishwanatham, Anil Kumar *Corros. Rev.* 23(2005) 181.
9. N. O. Eddy, E.E. Ebenso, U.J. Ibok, *J. Appl. Electrochem.* 40(2010) 445.
10. E.E. Ebenso, H. Alemu, S.A. Umoren, I.B.Obot, *Int. J. Electrochem. Sci.* 3(2008) 1325.
11. S.A. Umoren, I.B. Obot, E.E. Ebenso, N. O. Obi-Egbedi, *Int. J. Electrochem. Sci.* 3(2008) 1029.
12. M.A. Quraishi, D. Jamal *J. Appl. Electrochem* 32(2002) 425.
13. M. Abdallah *Portugaliae Electrochimica Acta* 22 (2004) 161
14. L. Anauda , R.A. Sathiyanathan, S.B. Maruthamuthu , M.C. Selvanayagam, S.B. Mohana, N.B. Palaniswamy *Indian Jour Chem Tech* 12(3) (2005) 356
15. H. Ashassi-Sorkhabi , B. Shaabani , B. Aligholipour , D. Seifzadeh *Appl Surf Sc* 252 (2006) 4039.
16. M.A. Bendahou , M.B.E. Benadellah , B.B. Hammouti *Pigment & Resin Technol* 35 (2006) 95
17. E.E. Ebenso , U.J. Ibok , U.J. Ekpe , S.A. Umoren , E. Jackson, O.K. Abiola , N.C. Oforka , S. Martinez *Trans SAEST* 39 (2004) 117
18. N.O. Eddy , 'Inhibition of corrosion of mild steel by some antibiotics' PhD Thesis, University of Calabar, Nigeria, 2008
19. N.O. Eddy , E.E. Ebenso *Afri J of Pure & Appl Chem* 2(6) (2008) 1

*20.* E.E. Ebenso , N.O.Eddy, A.O. Odiongenyi *Afri J of Pure & Appl Chem* 2(11) (2008) 107
21. K. Babic-Samardzija, C. Lupu , N. Hackerman , A.R. Barron , A. Luttge , *Langmuir* 21 (2005) 12187.
22. A. Popova, M. Christov, S. Raicheva, E. Sokolova *Corros. Sci.* 46(2004) 1333.
23. S.A. Odoemelam , N.O. Eddy *J Surf Sci Technol* 24 (1 & 2) (2008) 1.
24. S.A. Odoemelam , N.O. Eddy *J Mater Sci* 4(1) (2008) 1.
25. M. Abdallah *Corros Sci* 44 (2002) 717.
26. M. Abdallah *Corros Sci* 46 (2004) 1981.
27. M.M. El-Naggar *Corros Sci* 49(5) (2004) 2226.
28. R. Solmaz , G. Kardas , B. Yazici , M. Erbil *Protection of Metals* 41(6) (2005) 581.
29. W.T. Sing , C.L. Lee , S.L. Yeo , S.P.Lim , M.M. Sim *Bioorg Med Chem Lett* 11 (2001) 91.
30. A. El-Dissouky, A.A. El-Bindary, A.Z. El-Soubati, A.S. Hilali, *Spectrochim. Acta* ***A***57 (2001) 1163.
31. M. Ozcan , F. Karadag , I. Dehri *Colloids Surf A: Physi. Eng. Aspects* 316 (2008) 55.
32. G. Bereket , C. Ogretir , C. Ozsahim *J Mol Struct (THEOCHEM)* 66 (2004) 173
33. Y. Li , P. Zhao , Q. Liang , B. Hou *Appl Surf Sci* 252 (2005) 1245.
34. C. Ogretir , B. Mihci , G. Bereket *J Mol Struct (THEOCHEM)* 488 (1999) 223.
35. E.E. Ebenso , N.O. Eddy , A.O. Odiongenyi *Port. Electrochimica Acta* 27 (2009) 13.
36. S.A. Odoemelam , E.C. Ogoko, B.N. Ita, N.O. Eddy, *Port. Electrochimica Acta* 27 (2009) 57.
37. T. Arslan , F. Kandemirli , E.E. Ebenso , I. Love , H. Alemu *Corros Sci* 51 (2009) 35
38. N.O. Eddy, S.A. Odoemelam , P. Ekwumemgbo *Sci Res Essay* 4(1) (2009) 033.
39. N. O. Eddy, U. J. Ibok, E. E. Ebenso, A. El Nemr, and E. H. El Ashry , *J. Mol. Modelling.* 15 (2009)1085.
40. E.E. Ebenso, T. Arslan , F. Kandemirli , N. Caner , I. Love , *Int. Jour. Quantum Chem*. 110(2010) 1003.
41. M.J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D. J. Fox, T. Keith, M. A. Al- Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian 98, Revision A.7, Gaussian, Inc., Pittsburgh PA, 1998.
42. E. E. Oguzie, *Portugaliae Electrochimica Acta* 26(2008) 303.
43. E.E. Ebenso *Mater Chem Phys* 79 (2003) 58.
44. E.E. Ebenso *Bull. Electrochem* 19 (2003) 209.
45. E.E. Ebenso *Bull. Electrochem* 20 (2004) 55.
46. K. Dubey and G. Singh, *Portugaliae Electrochimica Acta* 25(2007) 249.
47. M.C. Essa, S.B. Maruthamuthu, M.A. Selvanayagam, N.B. Palaniswamy *J Indian Chem Soc* 2(4)(2005) 357.
48. Yurt , G. Bereket , A. Kivrak , A. Balaban , B. Erk *J Appl Electrochem* 35 (2005) 1025.
49. A.S. Fouda , F.E. Heakal , M.S. Radwan *J Appl Electrochem* 39(3)(2009) 391.
50. S.K. Rajappa , T.V. Venkatesha , B.M. Peaveen *Bull Mater Sci* 31(1) (2008) 37.
51. N. O. Eddy, S. A. Odoemelam , A. O. Odiongenyi, *J. Appl. Electrochem*. 39 (2009) 849.
52. H.M. Bhajiwala , R.T. Vashi *Bull Electrochem* 17 (2001) 441.
53. S. Bilgic , M. Sahin *Mater Chem Phys* 70 (2001) 290.
54. S.A. Umoren , O. Ogbobe , E.E. Ebenso *Bull Electrochem* 22 (2006) 155

55. E.E. Oguzie, B.N. Okolue , E.E. Ebenso, G.N. Onuoha, A.I.Onuchukwu *Mater Chem Phys* 87 (2004) 394.
56. G.K. Gomma *Mater Chem Phys* 55 (1998) 241.
57. S. A. Umoren, I. B. Obot and E. E. Ebenso, *E. J. Chem.* 5(2)(2008) 355 .
58. S.A. Umoren, O.Ogbobe, E.E. Ebenso and U.J. Ekpe, *Pigment and Resin Technol.* 35(5)(2006) 284.
59. H. Ashassi-Sorkhabi , B. Shaabani , D. Seifzadeh *Electrochimica Acta* 50 (2005) 3446
60. N. Khalil *Electrochimica Acta* 48 (2003) 2635.
61. J. Fang, J. Li *J Mol Struct (Theochem)* 593 (2002) 171.
62. B. Hasanov , M. Sadikoglu , S. Bilgic. *Appl Surf Sci* 253 (2007) 3913.
63. N.K. Allam *Appl Surf Sci* 253 (2007) 4570.
64. F. Kandemirli , S. Sagdina *Corros Sci* 49 (2007) 2118.
65. G. Bereket , C. Ogretir , C. Ozsahim *J Mol Struct (THEOCHEM)* 663 (2003) 39.
66. M. Ozcan , I. Dehri , M. Erbil *Appl Surf Sci* 236 (2004) 155
67. W. Li , Q. He , C. Pei , B. Hou *Electrochimica Acta* 52 (2007) 6386
68. M. Ozcan , I. Dehri ,M. Erbil *Prog Org Coating* 51 (2004) 181