ORIGINAL PAPER

Quantum chemical study of the inhibition of the corrosion of mild steel in H_2SO_4 by some antibiotics

**Nnabuk O. Eddy · Udo J. Ibok · Eno E. Ebenso ·
Ahmed El Nemr · El Sayed H. El Ashry**

Abstract The inhibition efficiency of some antibiotics against mild steel corrosion was studied using weight loss and quantum chemical techniques. Values of inhibition efficiency obtained from weight loss measurements correlated strongly with theoretical values obtained through semi empirical calculations. High correlation coefficients were also obtained between inhibition efficiency of the antibiotics and some quantum chemical parameters, including frontier orbital (E_{HOMO} and E_{LUMO}), dipole moment, log P, TNC and LSER parameters (critical volume and dipolar-polarisability factor), which indicated that these parameters affect the inhibition efficiency of the compounds. It was also found that quantitative structure activity relation can be used to adequately predict the inhibition effectiveness of these compounds.

N. O. Eddy (✉)
Department of Chemistry, Ahmadu Bello University,
Zaria, Kaduna, Nigeria
e-mail: nabukeddy@yahoo.com

U. J. Ibok
Department of Chemistry, University of Calabar,
Calabar, Nigeria

E. E. Ebenso
Department of Chemistry,
North West University (Mafikeng Campus),
Private Bag X2046,
Mmabatho 2735, South Africa

A. El Nemr
Environmental Division,
National Institute of Oceanography and Fisheries,
Alexandria, Egypt

E. S. H. El Ashry
Department of Chemistry, Faculty of Science,
Alexandria University,
Alexandria, Egypt

Introduction

Mild steel is one of the metals most widely used in industry. However, during some industrial processes (such as acid cleaning, etching, etc.) this metal corrodes easily, implying that the use of an inhibitor is necessary if the life of this valuable metal is to be protected [1–3].

The use of inhibitors is one of the most practical methods of protecting metals against corrosion [4–6]. It has been established that the initial mechanism involved in any corrosion inhibition process is adsorption of the inhibitor onto the surface of the metal [7, 8]. Corrosion inhibitors, which reduce the rate of corrosion of metals, are often synthesised from cheap raw materials or chosen from compounds that have centres for π-electron and functional groups (such as –C = C–, –OR, –OH, –NR_2, –NH_2 and –SR). These functional groups provide electrons that facilitate the adsorption of the inhibitor on the metal surface [7–10]. Research into the use of natural occurring substances has also been intensified [11]. Green corrosion inhibitors are preferred because they are environmentally friendly [4]. Recently, studies on the use of drugs have been reported by some researchers [12–15]. Most of these drugs are heterocyclic compounds and are found to be environmentally friendly; hence, they have great potential of as green corrosion inhibitors.

Although quantum chemical studies limit the corrosion inhibition efficiency with the molecular orbital energy levels of some organic compound, semi-empirical methods emphasize the approach involved in the selection of inhibitor. Therefore by correlating the experimental data with quantum chemical properties such as energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular

orbital (E_{LUMO}) and total negative charge (TNC), the behaviour of an organic inhibitor can be adequately studied [16–20]. The present study seeks to investigate the inhibitive properties of ampiclox (A), ampicillin (B), cloxacillin (C), chloramphenicol (D) and tetracycline (E) for mild steel corrosion using gravimetric and quantum chemical methods. The molecular structures of these compounds are shown below. From their molecular structures, it can be seen that these compounds contain hetero atoms in their aromatic structure; hence, they are expected to be good corrosion inhibitors.
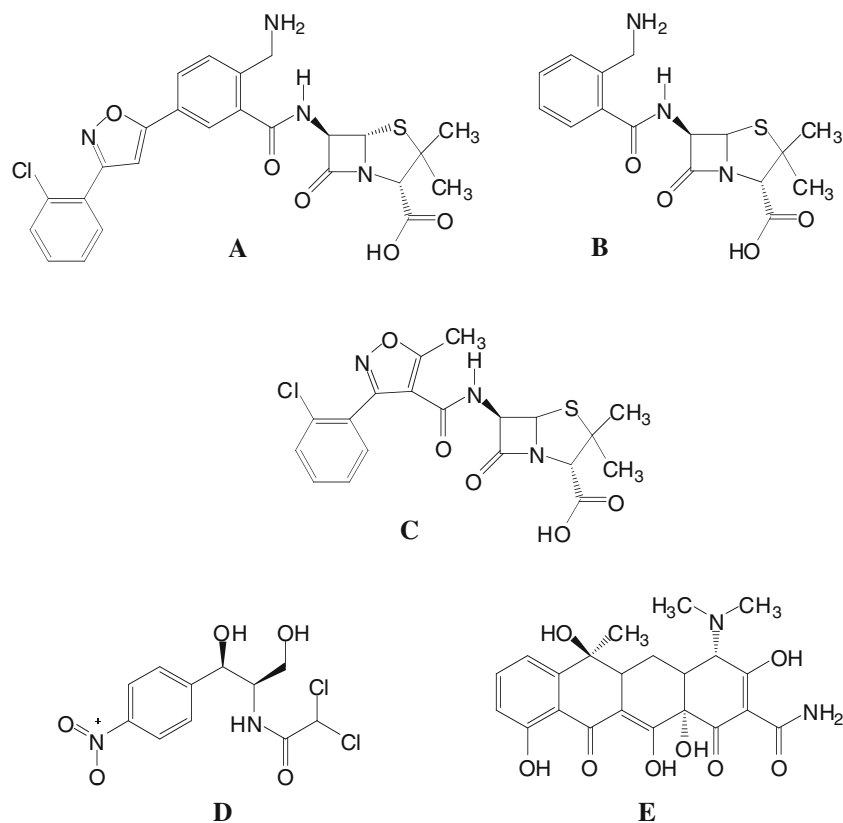
while the concentrations of the inhibitors (ampiclox, ampicillin, cloxacillin, chloramphenicol and tetracycline were 0.1, 0.2, 0.3, 0.4 and 0.5 g dm^{-3}, respectively. Each was dissolved in 0.1 M H$_2$SO$_4$.

Weight loss measurement

A previously weighed metal (mild steel) coupon was completely immersed in 250 ml test solution in an open beaker. The beaker was inserted into a water bath

Materials

Mild steel sheets of composition (wt %) Mn(0.6), P(0.36), C(0.15) and Si(0.03) were used in this study. The sheet was mechanically cut into coupons with dimensions 5×4× 0.11 cm. The coupons were degreased by washing in absolute ethanol, dried in acetone and stored in moisture-free desiccators before use [21, 22]. Analar grade reagents were used. These included concentrated tetraoxosulfate (VI) acid, sodium hydroxide and zinc dust.

Preparation of reagents

The concentrations of the various reagents used for this study were prepared using recommended methods. The concentrations of tetraoxosulfate (VI) acid used was 0.1 M,

maintained at a temperature of 313 K. The weight of the sample before immersion was measured using Scaltec high precision balance (Model SPB31; Scaltec Instruments, New York). At 24-h intervals, each sample was removed from the test solution, washed in a solution of NaOH containing zinc dust and dried in acetone before re-weighing.

The difference in weight for a period of 168 h was again taken as total weight loss. From weight loss measurements, inhibition efficiency (E_{exp}) and degree of surface coverage (θ) of the inhibitor were calculated using Eqs. 1 and 2,

$$E_{exp} = (1 - W1/W2) \times 100 \tag{1}$$

$$\theta = E_{exp}/100 \tag{2}$$

where E_{exp} is the experimental inhibition efficiency, and W_1 and W_2 are the weight losses (g dm^{-3}) of mild steel in the presence and absence of inhibitor, respectively.

Quantum chemical calculation

Quantum calculations were carried out using AM1 semi-empirical SCF-MO methods in the MOPAC 2000 program of CS ChemOffice packet program version 8 for Windows [23].

Calculations were performed on an IBM compatible Intel Pentium IV 2.8 GHz computer. All quantum theoretical calculations were started without any geometry constraints for full geometry optimisations using the program default calculation setting. The following quantum chemical indices, depending on the trial and error methods of solving the linear and non linear equations (using SPSS program; http://www.spss.com/) were considered: E_{HOMO}, E_{LUMO}, the dipole moment (μ) and TNC on the molecule, as well as the linear solvation energy relationships (LSER) parameters [intrinsic molecular volume (Vi) and dipolar-polarisability factor (π^*)]. To validate the correlations, calculations were carried out for the compound at a higher level of theory (B3LYP/6–31G**) using the Gaussian 2000 program (http://www.gaussian.com/). Statistical analyses were performed using SPSS program version 15.0 for Windows. Non-linear regression analyses were performed by unconstrained sum of squared residuals for loss function and estimation methods of Levenberg-Marquardt using SPSS program version 15.0 for Windows.

Results and discussion

Effect of concentration of the inhibitor

Figures 1, 2, 3, 4, and 5 show the variation in weight loss of mild steel with time upon corrosion of mild steel in H$_2$SO$_4$ containing various concentrations of A, B, C, D and E, respectively. It can be seen from the plots that weight loss of mild steel increases as the period of immersion increases, but decreases with increased concentration of inhibitor, indicating that the inhibition efficiencies of these compounds increase with increased concentration and that these compounds are adsorption inhibitors [24]. Table 1 shows the values of the experimental inhibition efficiencies of the inhibitors with increasing concentration at 313 K.

Values of degree of surface coverage calculated using Eq. 2 were used to fit curves for different adsorption isotherms, including Langmuir, Frumkin, Florry-Huggins, Temkin, Bockris-Swinkle and Freundlich adsorption isotherms. The results revealed that the adsorption of these inhibitors is best described by the Langmuir adsorption isotherm.
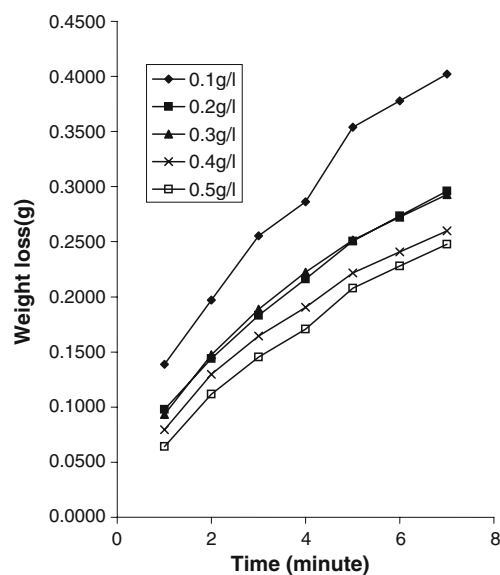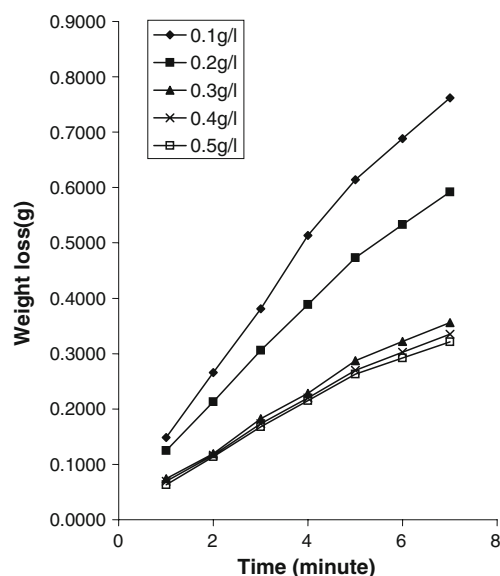

Fig. 1 Variation in weight loss with time during corrosion of mild steel in 0.1 M H$_2$SO$_4$ containing various concentrations of ampiclox at 313 K

Supposing the assumptions of the Langmuir adsorption isotherm are valid for the adsorption of the inhibitors on a mild steel surface, then Eq. 3 can be applied.

$$\theta = KC/(1 + KC) \tag{3}$$

where θ is the degree of surface coverage of the inhibitor, K is the equilibrium constant of adsorption of the inhibitor,

Fig. 2 Variation in weight loss with time during corrosion of mild steel in 0.1 M H$_2$SO$_4$ containing various concentrations of ampicillin at 313 K
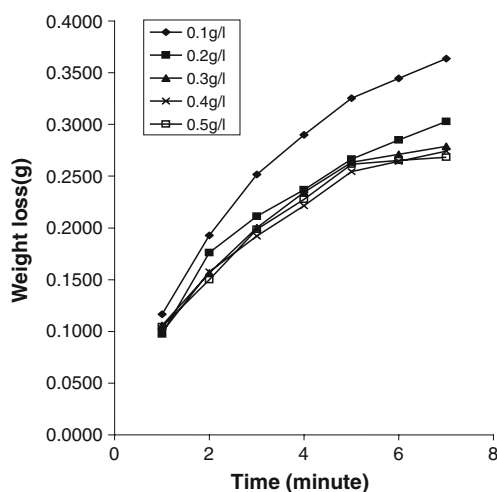
Fig. 3 Variation in weight loss with time during corrosion of mild steel in 0.1 M H_2SO_4 containing various concentrations of cloxacillin at 313 K

and C is the concentration of the inhibitor in the bulk electrolyte. Rearranging Eq. 3, Eqs. 4 and 5 are obtained:
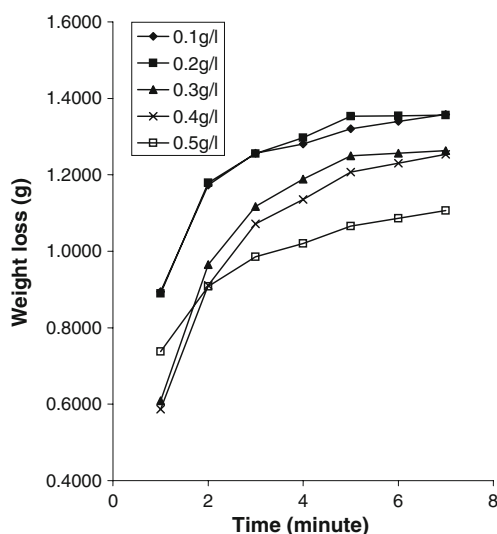
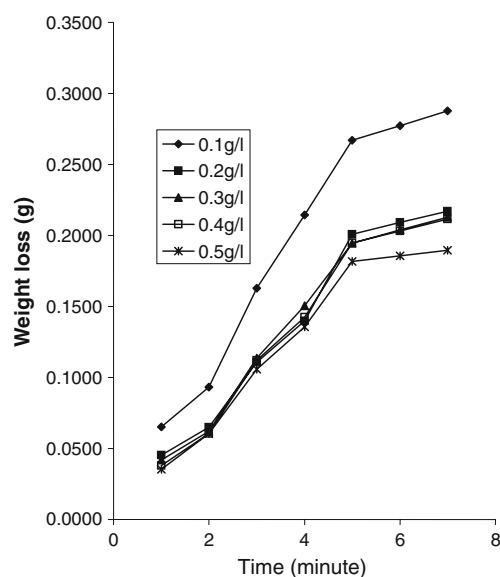$$\theta + \theta KC = KC \qquad (4)$$

$$C/\theta = 1/K + C \qquad (5)$$

Taking the logarithm of both sides of Eq. 5, Eq. 6 is obtained:

$$\log(C/\theta) = \log C - \log K \qquad (6)$$

Using Eq. 6, it was found that the plots of $\log(C/\theta)$ versus $\log C$ were linear, indicating that the assumptions of

Fig. 4 Variation in weight loss with time for corrosion of mild steel in 0.1 M H_2SO_4 containing various concentrations of chloramphenicol at 313 K

Fig. 5 Variation in weight loss with time for corrosion of mild steel in 0.1 M H_2SO_4 containing various concentrations of tetracycline at 313 K

Langmuir adsorption isotherm are valid for the adsorption of these inhibitors. Figure 6 shows the Langmuir isotherm for the adsorption of ampiclox, ampicillin, cloxacillin, chloramphenicol and tetracycline on the surface of mild steel. Values of Langmuir adsorption parameters deduced from the plots are recorded in Table 2.

The equilibrium constant of adsorption (K) is related to the free energy of adsorption as follows [25, 26]:

$$\Delta G_{ads} = -2.303 RT \log(55.5K) \qquad (7)$$

Values of free energy of adsorption calculated from Eq. 7 (using K values obtained from the Langmuir adsorption isotherm) are recorded in Table 2. The values are negative and less than the threshold value (-40 KJ mol^{-1}) required for chemical adsorption, indicating that adsorption of the inhibitors on mild steel surface is spontaneous and occurred according to the mechanism of physical adsorption.

Table 1 Values of experimental inhibition efficiency (E_{exp}) at 313 K of ampiclox (A), ampicillin (B), cloxacillin (C), chloramphenicol (D) and tetracycline (E)

Concentration (gdm^{-3})	A	B	C	D	E
0.1	76.08	54.75	78.41	19.14	82.92
0.2	82.43	64.87	82.02	19.36	87.12
0.3	82.61	78.86	83.45	25.02	87.31
0.4	84.29	80.11	83.72	25.56	87.45
0.5	85.57	80.93	84.07	34.33	88.75
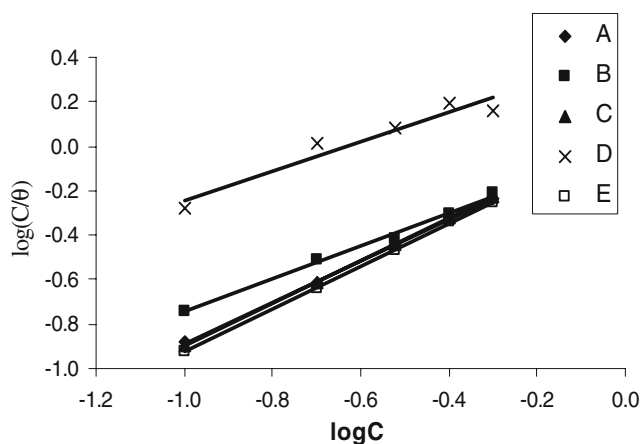
Fig. 6 Langmuir isotherm for the adsorption of ampiclox (*A*), ampicillin (*B*), cloxacillin (*C*), chloramphenicol (*D*) and tetracycline (*E*) on mild steel surface

Quantum chemical study

Quantitative structure activity relationships (QSAR) of the inhibitors A–E as inhibitors for the corrosion of steel in acidic medium were determined using the AM1 semi-empirical method and B3LYP/6–31G** at 313 K.

Tables 3 and 4 show the calculated quantum chemical properties for compounds A–E, E_{HOMO} (eV), E_{LUMO} (eV), μ (Debye), TNC, and critical volume and log P obtained from semi-empirical methods. E_{HOMO} is often associated with the electron-donating ability of a molecule, whereas E_{LUMO} indicates its ability to accept electrons [16–17]. The π^* has excellent correlation with the molecular dipole moments and comprises the overall information on induced dipole moment, polarisability and molecular volume, which are all essential in the transfer process of inhibitors from water to the metal surface. Polarisability is the ratio of induced dipole moment to the intensity of the electric field, i.e. induced dipole moment is proportional to polarisability, which increases with the increase in molecular volume [18].

Semi-empirical calculations for compounds A–E showed that the lowest energy of E_{HOMO} is for D, which has the lowest corrosion inhibition efficiency. Thus, inhibitor D has the lowest E_{exp} (%) and the value of E_{HOMO} in AM1 for

Table 2 Values of Langmuir adsorption parameters

Inhibitor	Slope	logk	R2	ΔGads
A	0.9313	0.0459	0.9930	−10.7030
B	0.7397	0.0054	0.9923	−10.4603
C	0.9564	0.0591	0.9998	−10.7821
D	0.6659	0.4228	0.9338	−12.9618
E	0.9620	0.0399	0.9998	−10.6670

this compound was −10.336 eV. This may decrease the adsorption of D on metal surfaces and consequently enhance the effect of acid on the surface leading to corrosion acceleration. On the other hand, the values of E_{HOMO} and μ increase as E_{LUMO} decreases in case of the other inhibitors with higher inhibition efficiency.

This is a consequence of the ease of transfer of electrons from HOMO to LUMO of metals. This may also facilitate adsorption and therefore inhibition by influencing the transport process [27].

An attempt to correlate some parameters calculated by AM1 with experimental corrosion inhibition efficiencies of the studied compounds reveals that there is no simple or direct relationship. This may be attributed to the complex nature of interactions in corrosion inhibition processes. Therefore, a composite index of more than one parameter that might affect the inhibition efficiency of a molecule may be correlated with its corrosion inhibition efficiency. Regression analysis was used to correlate inhibitor concentration (C_i) and LSER parameters with the average experimental inhibition efficiencies E_{exp} (%).

The linear model approximates corrosion inhibition efficiency (E_{cal} %) as presented in Eq. 8:

$$E_{cal} = Ax_jC_i + B \tag{8}$$

where A and B are constants obtained by regression analysis; x_j a quantum chemical index (E_{HOMO}, E_{LUMO}, π^*, etc) characteristic for the molecule j; C_i denotes the inhibitor concentration. Such a linear approach was found to be satisfactory for the correlation of the present results. Also, the non-linear model (NLM), proposed by Lukovits and co-workers for the study of the interaction of corrosion inhibitors with metal surfaces in acidic medium, was derived from Eq. 8 based on the Langmuir adsorption isotherm to give the following relationship [20].

$$E_{cal}(\%) = \frac{(Ax_i + B)C_i}{1 + (Ax_i + B)C_i} \times 100 \tag{9}$$

Equation 10 is the linear equation proposed for AM1 calculation. The non-linear equation proposed for AM1 calculation is Eq. 11. The linear equation proposed for B3LYP/6–31G** calculation is Eq. 12, while the non linear equation proposed for the B3LY/6–31G** calculation is Eq. 13

$$E_{cal}(\%) = -21.99 + 57.77 \times E_{LUMO} - 0.103$$
$$\times CrVol + 15.42 \times \log P + 24.88 \times C_i$$
$$- 67.08 \times TNC \tag{10}$$

Table 3 Calculated values of quantum chemical parameters of inhibitors A–E using MOPAC AM1 calculation in gas phase. E_{HOMO} Energy of the highest occupied molecular orbital, E_{LUMO} energy of the lowest unoccupied molecular orbital, TNC total negative charge, E_{L-H} LUMO−HOMO energy gap, μ dipole moment, V_i intrinsic molecular volume, π^* polar-polarisability factor, $Cr\text{-}Vol$ critical volume

Quantum parameter	A	B	C	D	E
V_i (cm³/M)	241.32	174.07	197.52	142.02	180.72
π^*	5.87	3.72	4.57	3.31	4.32
Cr-Vol (cm³ mol⁻¹)	1,314.5	885.5	1,057.5	824.8	1,131.5
logP	2.50	−0.06	2.43	−0.23	−3.85
E_{HOMO} (eV)	−7.5543	−8.11	−8.22	−10.34	−9.01
E_{LUMO} (eV)	−1.823	−1.419	−1.540	−1.107	−0.931
E_{L-H} (eV)	5.731	6.691	6.683	9.229	8.079
μ(Debye)	0.821	4.579	2.351	8.152	8.841
TNC	−4.465	−3.890	−3.843	−2.863	−4.942

(Correlation coefficient: $r^2=0.98$)

$$E_{cal}(\%) = \frac{(-1.407 + 55.67 \times E_{HOMO} + 55.084 \times \log P + 51.83 \times \mu - 59.24 \times TNC) \times Ci \times 100}{(1 + (-1.407 + 55.67 \times E_{HOMO} + 55.084 \times \log P + 51.83 \times \mu - 59.24 \times TNC) \times Ci)} \qquad (11)$$

(Correlation coefficient: $r^2=0.96$)

$$E_{cal}(\%) = 44.64 + 1036 \times E_{LUMO} + 13.07 \times \pi^*$$
$$+ 6.13 \times \mu + 24.88 \times C_i - 1.46 \times TNC \qquad (12)$$

(Correlation coefficient: $r^2=0.97$)

$$E_{cal}(\%) = \frac{(-21.36 + 0.277 \times Vi + 314.03 \times E_{LUMO} + 4.02 \times \mu + 1.01 \times TNC) \times Ci \times 100}{(1 + (-21.36 + 0.277 \times Vi + 314.03 \times E_{LUMO} + 4.02 \times \mu + 1.01 \times TNC) \times Ci)} \qquad (13)$$

(Correlation coefficient: $r^2=0.96$)

Values of E_{cal} calculated from Eqs. 10–13 are recorded in Table 5. For the non-linear method, multiple regressions were performed on inhibition efficiencies for compounds A–E at concentrations ranging from 0.1 to 0.5 g/L. The non-linear equation (Eq. 11) was obtained for AM1 where x_j is constructed as a composite index of E_{HOMO}, μ, TNC, and log P.

Calculated efficiencies (E_{cal} %) from Eq. 11 proposed for AM1 calculations for different concentrations of compounds A–E showed good correlation with experimentally obtained efficiencies (E_{exp} %)($r^2=0.96$) and the standard deviations were less than ±5.0.

The non-linear equation (Eq. 13) proposed for B3LYP/ 6–31G** calculations for compounds A–E has a correlation coefficient (r)=0.96 and the standard deviations were less than ±5.68, where x_j in Eq. 9 represents a composite index of selected quantum parameters (E_{LUMO}, μ, TNC and LSER parameter V_i).
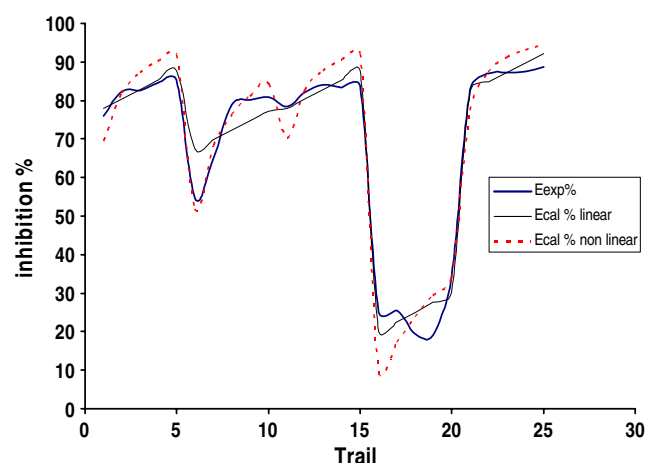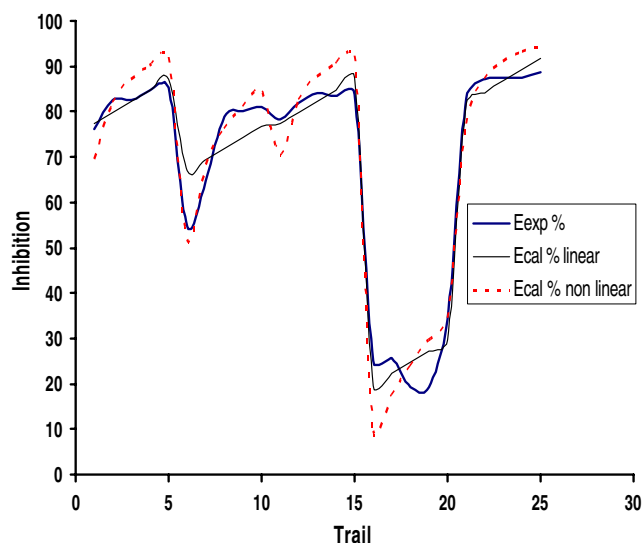
The E_{cal} (%) obtained for both models correlated strongly with the E_{exp} (%) ($r^2=0.98$ and 0.96). It is evident

Table 4 Quantum chemical parameters of inhibitors A–E using gas phase B3LYP/6–31G*. E_{HOMO} Energy of the highest occupied molecular orbital, E_{LUMO} energy of the lowest unoccupied molecular orbital, E_{L-H} LUMO−HOMO energy gap, μ dipole moment, TNC total negative charge, V_i intrinsic molecular volume, π^* polar-polarisability factor

Quantum parameter	A	B	C	D	E
V_i (cm³/M)	241.32	174.07	197.52	142.02	180.72
π^*	5.87	3.72	4.57	3.31	4.32
E_{HOMO} (eV)	−0.2239	−0.2178	−0.2422	−0.2717	−0.2167
E_{LUMO} (eV)	−0.0648	−0.0420	−0.0492	−0.1057	−0.0989
E_{L-H} (eV)	0.159	0.176	0.193	0.166	0.118
μ(Debye)	1.6778	1.0579	2.7218	5.3735	11.3529
TNC	−6.950	−5.612	−3.286	−4.034	−7.481

Table 5 Calculated values of inhibition efficiency for the inhibitors (E_{cal})

Concentration (g/l)	Eq. 10	Eq. 11	Eq. 12	Eq. 13
Ampiclox				
0.1	77.87	69.41	77.20	69.45
0.2	80.35	81.94	79.70	81.97
0.3	82.84	87.19	82.20	87.21
0.4	85.33	90.07	84.70	90.09
0.5	87.82	91.90	87.20	91.91
Ampicillin				
0.1	67.36	51.64	66.90	51.71
0.2	69.85	68.11	69.40	68.17
0.3	72.34	76.21	71.90	76.26
0.4	74.83	81.03	74.40	81.07
0.5	77.31	84.22	76.90	84.26
Cloxacillin				
0.1	77.87	70.36	77.40	70.38
0.2	80.35	82.60	79.81	82.61
0.3	82.84	87.69	82.32	87.70
0.4	85.33	90.47	84.80	90.48
0.5	87.82	92.23	87.33	92.24
Chloramphenicol				
0.1	20.12	9.39	19.20	9.50
0.2	22.61	17.17	22.20	17.35
0.3	25.10	23.72	24.70	23.95
0.4	27.59	29.31	27.20	29.58
0.5	30.08	34.14	29.70	34.43
Tetracycline				
0.1	82.29	77.34	81.72	99.35
0.2	84.78	87.22	84.23	87.23
0.3	87.27	91.10	86.71	91.11
0.4	89.76	93.17	89.22	93.18
0.5	92.24	94.46	91.71	94.47

Fig. 8 Plot of experimental and calculated (B3LYP/6–31G**) inhibitor efficiency of compounds A–D at different concentrations

Fig. 7 Plot of experimental and calculated (AM1) inhibitor efficiency of compounds A–D at different concentrations

from the above that frontier orbital (E_{HOMO} and E_{LUMO}), dipole moment, log P, TNC and LSER parameters affect the inhibition efficiency of compounds A–E as shown by the high correlation coefficient factors for the proposed equations. However, it should be pointed out that factors derived from competitive adsorption, the nature of the surface and the solubility constant may contribute to the establishment of better relationships. The poor solubility of compounds may be one of the reasons for the unpredictability of the inhibition efficiencies of inhibitors.

In order to validate correlations between quantum parameters calculated for compounds A–E and their experimental inhibition efficiencies, an optimised structure calculations were carried out using B3LYP/6–31G** as a higher level of theory (Table 4). The linear and non-linear multiple regressions performed on inhibition efficiencies and quantum parameters obtained by optimised structure calculations using B3LYP/6–31G** gave linear Eq. 12 and non-linear Eq. 13. Figures 7 and 8 represent the pattern of E_{exp} (%) and E_{cal} (%) obtained by the linear and non-linear models proposed for B3LYP/6–31G** calculation data.

Calculated efficiencies (E_{cal} %) obtained from these equations at different concentrations of compounds A–E showed good correlations with experimental efficiencies (E_{exp} %), with correlation coefficients (r)=0.97 and 0.96 for the linear and non-linear models, respectively. Also, the standard deviations were less than ±5.68.

Conclusions

From the results of this study, we conclude that ampiclox, ampicillin, cloxacillin, chloramphenicol and tetracycline are

good inhibitors for the corrosion of mild steel. The mechanism of adsorption of the inhibitors on the surface of mild steel is by physical adsorption and is consistent with adsorption model of Langmuir. Quantum chemical parameters such as E_{HOMO} (eV), E_{LUMO} (eV), μ (Debye), TNC, critical volume and log P are vital in studying the inhibition effectiveness of the inhibitor. The study also revealed that QSAR can be applied to the study of the effectiveness of the inhibitors. However, it may be used to define an optimal group of parameters that might predict the structure and the suitability of the molecules as inhibitors. The quantum mechanical approach may also be applied to predict molecules or structures that are better for corrosion inhibition purposes if it is considered that the effect depends only on the properties of the inhibitor molecule.

References

1. Ebenso EE (2003) Bull Electrochem 19(5):209–216
2. Ebenso EE (2003) Mater Chem Phys 79:58–70
3. El Ashry HE, El Nemr A, Esawy SA, Ragab S (2006) Electrochim Acta 51:3957–3968
4. Eddy NO, Ebenso EE (2008) Afr J Pure Appl Chem 2(6):046–054
5. Odoemelam SA, Eddy NO (2008) J Surface Sci Technol 24(1–2):1–14
6. Odoemelam SA, Eddy NO (2008) J Mater Sci 4:87–96
7. Ashassi-Sorkhabi H, Shaabani B, Seifzadeh D (2005) Electrochim Acta 50:3446–3452
8. Eddy NO, Odoemelam SA, Odiongenyi AO (2009) J Appl Electrochem (in press). doi 10.1007/s10800-008-9731-z
9. Okafor PC, Ebenso EE (2007) Pigment and Resin Technol 36 (3):134–140
10. Okafor PC, Osabor VI, Ebenso EE (2007) Pigment and Resin Technol 36(5):299–305
11. Ebenso EE, Eddy NO, Odiongenyi AO (2008) Afri J Pure Appl Chem 2(11):107–115
12. Abdallah M (2004) Corros Sci 46:1981–1996
13. Abdallah M (2002) Corros Sci 44:717–728
14. Eddy NO, Ekwumemgbo P, Odoemelam SA (2008) Int J Phys Sci 3(11):275–280
15. Eddy NO, Odoemelam SA, Mbaba AJ (2008) Afri J Pure Appl Chem 2(12):132–138
16. El Ashry HE, Khamis E, Ibrahim AK (2000) Br Corros J 35: 150–164
17. El Ashry HE, El Nemr A, Esawy SA, Ragab S (2006) J Phys Chem 1:41–55
18. Karelson M, Lobanov S (1996) Chem Rev 96:1027–1043
19. Lukovits L, Shaban A, Kalman E (2003) Russ J Electrochem 19 (2):177–181
20. Lukovits I, Bako I, Shaban A, Kalman E (1998) Electrochim Acta 43:131–135
21. Agrawal YK, Talati JD, Shah MD, Desai MN, Shah NK (2003) Corros Sci 50:2310–2317
22. Jovancicervic V, Ramachadran S, Prince P (1999) NACE Int 55 (5):449–453
23. Wang H, Wang X, Wang H, Wang L, Liu A (2007) J Mol Model 13:147–153
24. Eddy NO, Ekop AS (2008) J Mater Sci 4(1):10–16
25. Ebenso EE (2004) Bull Electrochem 12:551–559
26. Okafor PC, Ikpi MI, Uwah IE, Ebenso EE, Ekpe UJ, Umoren SA (2008) Corros Sci. doi:10.1016/j.corsci.2008.05.009
27. Lebrini M, Bentiss F, Vezin H, Langreenee M (2006) Corros Sci 48:1279–1291