ADSORPTION AND QUANTUM CHEMICAL STUDIES OF THE INHIBITIVE PROPERTIES OF TETRACYCLINE FOR THE CORROSION OF MILD STEEL IN 0.1 H_2SO_4

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Abstract

The inhibitory potentials of tetracycline for the corrosion of mild steel was investigated using gravimetric, thermometric, gasometric and quantum chemical approaches. Results obtained from gravimetric, gasometric and thermometric measurements indicates that the average inhibition efficiency of tetracycline (at 303, 313, 323 and 333 K) ranged from 85.78 to 95.52 %, 65.58 to 86.49 % and from 56.52 to 93.17 % respectively. The activation and free energies for the inhibition reactions supported the mechanism of physical adsorption. The adsorption of tetracycline on mild steel surface is endothermic,

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spontaneous and is consistent with the Langmuir type of adsorption. Quantum chemical study reveals that the calculated values of the frontier orbital energies are within the limits reported for some adsorption inhibitors. Also, the sites for nucleophilic and electrophilic attacks are in the hydroxyl bonds, (O23) and (O26) respectively.

Keywords: corrosion; inhibition; tetracycline; DFT study

Resumen

La potencial capacidad inhibitoria de la tetraciclina para la corrosión del acero fue investigada usando análisis gravimétrico, termométrico, gasométrico y química cuántica. Los resultados obtenidos en las mediciones gravimétricas, gasométricas y termométricas indican que la eficiencia promedio de inhibición de la tetraciclina (a 303 K) se encuentra en el rango de 85.78 a 95.52%, 65.58 a 86.49% y 56.52 a 93.17% respectivamente. La activación y las energías de libre para las reacciones de inhibición apoyan el mecanismo de adsorción física. La adsorción de tetraciclina en superficies de acero templado es endotérmica, espontánea y es consistente con una tipo Langmuir. El estudio cuántico reveló que los valores calculados de las energías de orbital de frontera están dentro de los límites que se informaron para algunos inhibidores de adsorción. Además, los sitios para los ataques nucleofílicos y electrofílicos se encuentran en los enlaces hidroxilo (O23) y (O26) respectivamente.

Palabras clave: corrosión; inhibición, tetraciclina; estudio DFT

Introduction

Corrosion inhibitors are either synthesized from cheap raw materials or are chosen from organic compounds containing electronegative functional groups and π-electrons, triple or conjugated double bonds. For the last class of inhibitors, the presence of heteroatoms (such as sulphur, oxygen, nitrogen) as well as aromatic rings in their structures facilitate the adsorption of the inhibitor on the metal surface (which is the initial mechanism for the inhibition of the corrosion of metal) [1-2]. Base on the above listed criteria, several inhibitors have been synthesized for the inhibition of the corrosion of metals (including mild steel) [2-5]. Also, extract of some naturally occurring products have been found to be good inhibitors (green inhibitors) [6-14]. Perhaps, the major advantages of green inhibitors are their environmentally friendly or non toxic nature, the ease of accessibility and low cost. However, the chemistry of most green corrosion inhibitors has not been fully explored because their inhibitory potential is due to synergistic effect of some of its phytochemical constituents. Consequently, determination of their quantum chemical parameters and molecular properties may not be feasible. In the light of these and other factors, the uses of some penicillin compounds as corrosion inhibitors have been given wider considerations because most of them have the potentials of competing with green inhibitors [14-22].

Recently, quantum chemical calculations have been found to be one of the most powerful tools for studying the mechanism of inhibition of the corrosion of metals by organic inhibitors [23-26]. For example Eddy *et al.* [27] found excellent correlation between inhibition efficiency and some quantum chemical parameters (namely, dipole moment, E_{HOMO}, E_{LUMO}, $E_{LUMO-HOMO}$, polarizability factors), El Ahry *et al.* [28-29] also found that the inhibition efficiency of some organic inhibitors increases with increasing value of the E_{HOMO} but decreases with increasing values of the E_{LUMO} and suggested that quantitative activity relationship can be used to predict the probably behaviour of some organic inhibitors. Khaled [30] stated that the inhibitory behaviour of some triazoles for the corrosion of mild steel can be explained using molecular simulation, quantum chemical calculations and electrochemical studies. Asshasi-Sorkhabi *et al.* [31], also supported their experimental findings on the inhibitory action of some pyrimidinic Schiff bases (for the corrosion of mild steel) using quantum chemical principles. Of specific interest in the field of quantum chemical study is the subject of the Density functional theory (DFT). The premise behind the DFT is that the energy of a molecule can be determined from electron density instead of a wave function [32]. The extension of DFT principles in studying the inhibition of the corrosion of mild steel has been reported by Wang *et al.* [33], Xia *et al.* [34], Gomez *et al.* [35] and others.

The present study is aimed at investigating the inhibitory and adsorption properties of tetracycline for the corrosion of mild steel using experimental and theoretical approaches. Tetracyclines are a large family of compounds that were discovered as natural products by Benjamin Minge Duggar and first described in 1948. Under Yellapragada subbarao, Benjamin Duggar made his discovery of the world's first tetracycline antibiotic, Aureomycin, in 1945. tetracycline was also discovered by Lioyd Conover in the research departments of Pfizer. The primary use of tetracycline is for the treatment of *acne vulgaris* and *rosacea*. It is first-line therapy for Rocky Mountain Spotted Fever (Rickettsia), Q Fever (Coxiella) Psittacosis and Lymphogranuloma venereum (Chlamydia), and to eradicate nasal carriage of meningococci [36]. From our knowledge, tetracycline has not been used as an inhibitor for the corrosion of mild steel in H_2SO_4. The chemical and optimised structures of tetracycline are shown in Figure 1. The molar mass of tetracycline is 444.44 g/mol and its chemical formula is $C_{22}H_{24}N_2O_8$. It has five -OH bonds, three C=O bonds and one $-NH_2$ bond. Therefore, tetracycline is enriched with π-electrons and hetero atoms suggesting that the molecule may be a good corrosion inhibitor.
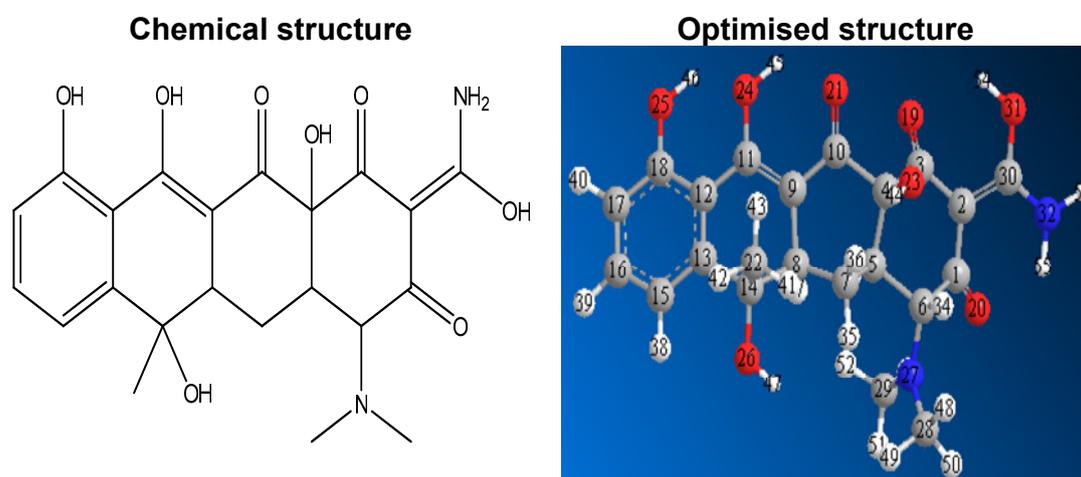
Figure 1. Chemical and optimized structure of tetracycline.

Experimental techniques

Materials

Materials used for the study were mild steel sheet 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 into 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 (tetracycline) was supplied by LIVEMOORE Chemical Company, Ikot Ekpene, Akwa Ibom State, Nigeria and was used without further purification. The concentrations of the inhibitors used for the study were $3x10^{-4}$ to $11 x10^{-4}$M.

Gravimetric method

In the gravimetric experiment, a previously weighed metal (mild steel) coupon was completely immersed in 250ml of the test solution (0.1 M H_2SO_4) in an open beaker. The beaker was inserted into a water bath maintained at 303 K. After every 24hours, each coupon was withdrawn from the test solution, washed in a solution containing 50% NaOH and 100g/l of zinc dust. The washed steel coupon was rinsed in acetone and dried in air. The difference in weight for a period of 168h 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 (CR) were calculated using equations 1,2 and 3 respectively [37];

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

$$\theta = \left(1 - \frac{W_1}{2}\right) \qquad (2)$$

$$CR = \frac{W}{At} \qquad (3)$$

where W_1 and W_2 are the weight losses (g) for mild steel in the presence and absence of the inhibitor 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.

Gasometric method

Gasometric methods were carried out at 303 K, using 2.5 M H_2SO_4 as the blank. Mild steel coupon was introduced into a test solution in the gasometric flask. The flask was properly covered and the volumes of hydrogen gas evolved per minutes were recorded until constant values were obtained. From the volume of hydrogen evolved per minute, inhibition efficiencies were calculated using equation 4 [38].

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

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.

Thermometric method

This was also carried out as reported elsewhere [39]. From the rise in temperature of the system per minute, the reaction number (RN) was calculated using equation 5:

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

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 as follows:

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

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 the inhibitors.

Computational aspects

The molecular diagrams of tetracycline were drawn using the Chem3D package in the ChemOffice suite. All the quantum calculations were performed with complete geometry optimization. Semiempirical parameters were calculated using MOPAC 2008 software [34]. Ab initio parameters were calculated using the GAMESS software. The basis set used for the calculations was the density functional theory (DFT) method at the level of B3LYP/ 6-31G (d,p).[40-42].
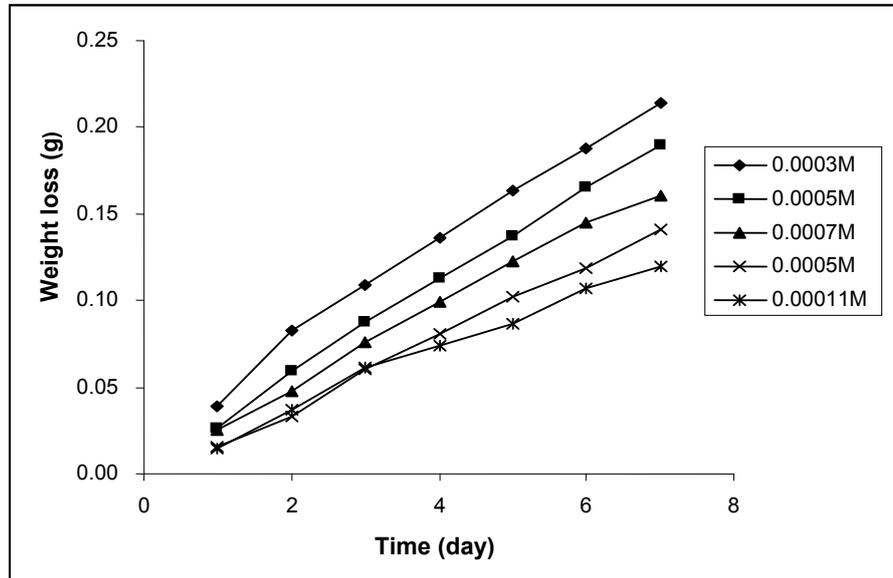
Results and discussions

Effect of concentration of tetracycline

Figure 2 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 tetracycline at 303 K. From Figure 2, it is evident that weight loss of mild steel increases with increasing period of contact but decreases with increasing concentration of tetracycline indicating that the rate of corrosion of mild steel in H_2SO_4 solution increases with increasing period of contact but decreases with increase in the concentration of tetracycline. This also suggests that tetracycline inhibited the corrosion of mild steel in 0.1 M H_2SO_4. At higher temperatures (313, 323 and 333 K), similar plots were obtained (plots not shown). However, weight loss of mild steel was found to increase with increasing temperature which also suggests that the rate of corrosion of mild steel in H_2SO_4 solutions increases with increasing temperature and that the inhibition efficiency of tetracycline for mild steel corrosion decreases with increasing temperature, a trend that supports the mechanism of physical adsorption. It has been established that the mechanism of chemical adsorption is characterized by increase in the values of inhibition efficiency with increasing temperature. On the other hand, decreasing values of inhibition efficiency with increasing temperature portrays the mechanism of physical adsorption, as indicated in the present study.

We also used gasometric and thermometric methods to study the inhibitive effect of tetracycline for mild steel corrosion. The results obtained reveal that the rate of hydrogen evolution (for gasometric method) and the rate of change in temperature (for thermometric method) increases with increasing period of contact but decreases with increasing concentration of tetracycline. These also confirm that tetracycline is an inhibitor for the corrosion of mild steel in H_2SO_4 solutions.

In order to further validate the results of our study, we calculated values of the corrosion rates of mild steel in H_2SO_4 solutions and also the inhibition efficiencies of tetracycline for the corrosion of mild steel in various media and presented the results in Table 1. From the results obtained, it is evident that the corrosion rate of mild steel decreases with increasing concentration of tetracycline but increases with increase in temperature. The results also indicate that values of inhibition efficiency obtained from weight loss measurements are relatively higher than those obtained from hydrogen evolution and thermometric methods implying that the average inhibition efficiency of tetracycline is better than its instantaneous inhibition efficiency. These findings arise

from the fact that gasometric and thermometric methods measure instantaneous inhibition efficiency while weight loss method measures average inhibition efficiency [43].

Figure 2. Variation of weight loss with time for the corrosion of mild steel in 0.1 M H_2SO_4 containing various concentrations of tetracycline.

Adsorption and thermodynamic considerations

The logarithm form of Arrhenius equation (equation 7) was used to calculate the activation energy for the corrosion of mild steel in the presence of tetracycline:

$$logCR = logA - E_a/2.303RT \qquad (7)$$

From equation 7 the plot of logCR versus 1/T should be a straight line with slope equal to -$E_a/2.303R$. Figure 3 shows the Arrhenius plots for the corrosion of mild steel in solutions of HCl. Values of E_a calculated from slopes of the plots are recorded in Table 2. These values ranged from 28.88 to 47.16 J/mol (E_a for the blank = 25.57 J/mol) indicating that the corrosion of mild steel is retarded by the presence of tetracycline [44]. The results also indicate that the activation energy increases with increasing concentration of tetracycline which suggests that there is increasing ease of adsorption of the inhibitor with increasing concentration. The activation energies are also lower than the threshold value of 80 kJ/mol required for the mechanism of chemical adsorption. Therefore, the adsorption of tetracycline on mild steel surface supports the mechanism of physical adsorption [45].

In order to calculate thermodynamic parameters for the adsorption (ΔH_{ads} and ΔS_{ads}) of tetracycline on mild steel surface, the transition state equation (Equation 8) was used [46]:

$$log(CR/T) = log(R/Nh) + \Delta S_{ads}/2.303R - \Delta H_{ads}/2.303RT \qquad (8)$$

Table 1. Corrosion rates of mild steel and inhibition efficiency of tetracycline for the corrosion of mild steel in 0.1M H_2SO_4.

C (mol/dm³)	Inhibition efficiency (%I)				Corrosion rate (gcm⁻²h⁻¹) x 10⁻⁵				Inhibition efficiency (%I)	
	303 K	313 K	323 K	333 K	303 K	313 K	323 K	333 K	T (303 K)	G (303 K)
3 x 10⁻⁴	85.78	82.92	71.93	51.77	6.38	8.56	12.5	24.9	65.58	56.52
5 x 10⁻⁴	87.36	87.12	77.06	67.27	5.66	6.46	10.2	14.1	70.82	63.36
7 x 10⁻⁴	90.60	87.31	77.06	72.79	4.77	6.33	8.14	16.9	79.20	64.60
9 x 10⁻⁴	92.06	87.45	84.57	73.89	4.21	6.29	1.95	13.5	84.24	73.91
11 x 10⁻⁴	95.52	88.75	95.63	78.46	3.55	5.64	6.88	11.1	86.49	93.17

** T = data obtained from thermometric analysis and G = data obtained from gasometric analysis.
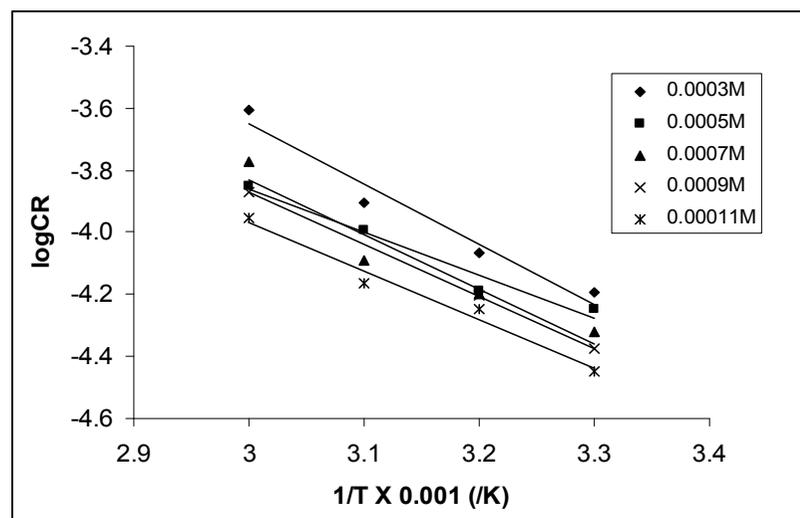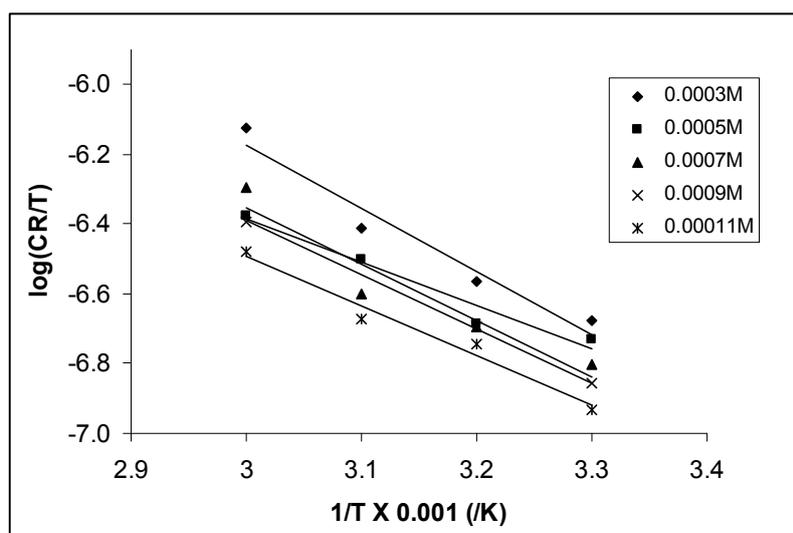

Figure 3. Plots of logCR versus 1/T for the corrosion of mild steel in 0.1 M H_2SO_4 containing various concentrations of tetracycline.

From equation 8, a plot of logC(R/T) versus 1/T should give a straight line with the slope and intercept equal to $-\Delta H/2.303R$ and $[\log(R/Nh) + \Delta S/2.303R]$ respectively. Figure 4 shows the transition state plot for the corrosion of mild steel in the presence of tetracycline. Values of ΔS_{ads} and ΔH_{ads} calculated from equation 8 are recorded in Table 2. The large negative values of ΔS_{ads} and positive values of ΔH_{ads} indicate that the corrosion of mild steel inhibited by tetracycline is endothermic and that it is controlled by activation complex. We also observed that values of E_a and ΔH_{ads} correlated strongly (r = 0.9878). This can be explained as follows. The enthalpy change of a reaction can be represented as $\Delta H_{ads} = E_a + PdV$. For reactions involving liquids, dV is negligible implying that values of ΔH_{ads} should be comparable with those of E_a.

Table 2. Thermodynamic parameters for the adsorption of tetracycline on mild steel surface.

C (moldm^3)	E_a (Jmol^{-1})	R^2	ΔH_{ads} (Jmol^{-1})	ΔS (Jmol^{-1})	R^{2*}
3 x 10^{-4}	47.16	0.9603	34.55	-153.67	0.9954
5 x 10^{-4}	37.16	0.9416	30.73	-212.18	0.9367
7 x 10^{-4}	31.29	0.9642	28.67	-228.38	0.9566
9 x 10^{-4}	29.80	0.9165	27.18	-232.77	0.9009
11 x 10^{-4}	28.88	0.9952	26.26	-239.38	0.9251

Figure 4. Plots of log(CR/T) versus 1/T for the corrosion of mild steel in 0.1 M H$_2$SO$_4$ containing various concentrations of tetracycline.

In order to study the adsorption characteristics of tetracycline on mild steel surface, calculated values of degree of surface coverage were used to fit curves for different adsorption isotherms including Langmuir, Temkin, Bockris-Swinkle, Flory-Huggins, Freundlisch and Frumkin adsorption isotherms. The tests revealed that Langmuir adsorption isotherms best described the adsorption characteristics of tetracycline. Langmuir isotherm equation relates the degree of surface coverage (θ) with the concentration of the inhibitor in the bulk electrolyte as follows [47],

$$C/\theta = 1/K_{ads} + C \qquad (9)$$

where K_{ads} is the equilibrium constant of adsorption. Figure 5 shows Langmuir isotherm for the adsorption of tetracycline on mild steel surface. Values of adsorption parameters deduced from the Langmuir plots are recorded in Table 3. From the results obtained, the slopes and R^2 values are very close to unity indicating a strong adherence of the adsorption data to the assumptions of Langmuir isotherm.

The free energy of adsorption (ΔG_{ads}) of tetracycline on mild steel surface was calculated using the following equation [48],

$$\Delta G_{ads} = -2.303RT\log(55.5K) \qquad (10)$$

where K is the equilibrium constant of adsorption obtained from Langmuir isotherms, θ is the degree of surface coverage of the inhibitor. Calculated values of ΔG_{ads} are also presented in Table 3. From the results obtained, the free energies are negatively less than the threshold value (-40 KJ/mol) required for chemical adsorption indicating that the adsorption of tetracycline on mild steel surface is spontaneous and supports the mechanism of physical adsorption [49].
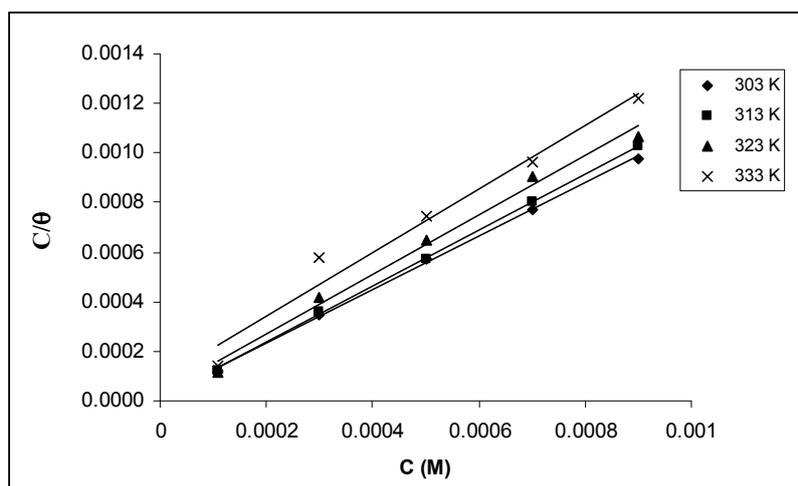
Figure 5. Langmuir isotherm for the adsorption of tetracycline on mild steel surface.

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

Temperature (K)	logK	slope	ΔG_{ads} (KJ/mol)	R^2
303	0.0074	0.9361	-10.14	0.9995
313	0.0399	0.962	-10.33	0.9998
323	0.0032	0.8474	-10.11	0.9907
333	0.0210	0.7509	-10.22	0.9932

Synergism

Synergism is a combined action of a compound greater in total effect than the sum of individual effects. It has become one of the most important factors in inhibition process and serves as a basis for all modern corrosion inhibitor formulation. Synergism of corrosion inhibitors is either due to interaction between components of the inhibitors or due to interaction between the inhibitor and one of the ions present in aqueous solution [50].

Synergistic parameters for joint adsorption of tetracycline and halides were calculated using equation 11[51]

$$S = \frac{1 - \eta_A - \eta_B + \eta_A\eta_B}{1 - \eta_{AB}} \quad (11)$$

where η_A and η_B are inhibition efficiencies of compound A and B respectively; η_{AB} is the inhibition efficiency of a combination of two inhibitors. Table 4 presents values of the inhibition efficiency of various concentrations of tetracycline, co-employed with 0.06 M halides (KBr, KI and KCl) respectively. The results show some improvements in the inhibition efficiency of tetracycline for the corrosion of mild steel in H_2SO_4 solutions. The synergistic parameters for the joint combination of tetracycline and halides are presented in Table 5. The results reveal that at 303K, combinations of tetracycline with 0.06MKBr and KCl lead to enhancement in inhibition efficiency of tetracycline. Since values of S calculated for each set of pair of combination are greater than unity, it can be deduced that enhancement in inhibition efficiency is due to interaction between molecules of tetracycline and these halides. On the other hand, combinations of 0.06 M KI with different concentrations of tetracycline resulted in inhibition efficiencies less than those of tetracycline or KI indicating that there is no synergism between tetracycline and 0.06MKI and that adsorption of tetracycline is antagonistic to that of KI and vice versa. However, at tetracycline concentration of 9×10^{-4} M, adsorption of tetracycline was found to be independent of the adsorption of KI (S<0). At 333 K, combinations of different concentrations of tetracycline with 0.06MKBr and 0.06 M KCl respectively exhibited synergistic effect implying that enhancement in inhibition efficiency is due to interaction between molecules of tetracycline and these halides(KCl).

Table 4. Inhibition efficiency of tetracycline co-employed with halides**.**

C (mol dm^{-3})	KBr		KI		KCl	
	303 K	333 K	303 K	333 K	303 K	333 K
3×10^{-4}	94.43	84.91	15.13	30.25	95.72	84.63
5×10^{-4}	94.81	86.56	29.38	32.55	96.41	88.32
7×10^{-4}	95.01	86.96	32.12	32.73	98.42	87.99
9×10^{-4}	95.17	87.37	44.86	42.46	98.42	88.89
11×10^{-4}	95.92	88.81	45.18	44.81	98.90	95.43

Table 5. Synergistic parameters for the joint adsorption of tetracycline and halides on mild steel surface.

C (moldm^{-3})	303 K			333 K		
	KBr + tetra	KI + tetra	KCl + tetra	KBr + tetra	KI + tetra	KCl + tetra
3×10^{-4}	3.80	0.17	28.19	6.71	0.27	7.02
5×10^{-4}	2.78	0.27	33.36	6.78	-0.04	21.38
7×10^{-4}	0.63	0.11	103.72	6.96	0.00	8.70
9×10^{-4}	7.48	-0.69	75.02	6.95	0.15	7.66
11×10^{-4}	8.21	0.15	74.09	7.56	0.02	7.04

Interestingly, we observed that the joint adsorption of tetracycline is also consistent with the Langmuir type adsorption and that some thermodynamic and adsorption parameters of tetracycline are modified by the presence of the halides. For example, there was a slight reduction in the values of E_a when tetracycline was combined with 0.06 M KBr (11.26 J/mol), KI (28. 01J/mol) and KCl (18.23 J/mol) respectively. The average values of the enthalpy change were 29.79, -5.33 and 46.54 J/mol for the joint adsorption of tetracycline with 0.06 M KBr, KI and KCl respectively. From values of Langmuir adsorption parameters (Table 6) obtained (Langmuir plots not shown) for the joint adsorption of tetracycline and halides, we observed significant improvement in the adsorption

behavior of tetracycline. These modifications in adsorption and thermodynamic parameters due to the joint adsorption of tetracycline and halides indicate that the halides enhanced the adsorption behavior of tetracycline.

Table 6. Langmuir parameters for joint adsorption of tetracycline and halides on mild steel surface.

System	Temperature(K)	Slope	K	R^2	ΔG_{ads}
KBr	303	0.9917	0.0047	1.0000	10.11
	333	0.9754	0.00187	1.0000	10.20
KI	303	0.5982	1.1400	0.9576	16.71
	333	0.7565	0.3443	0.9697	12.09
KCl	303	0.9782	0.0598	1.0000	10.44
	333	0.9985	0.1365	0.9985	10.89

Quantum chemical and DFT study

Global reactivity

The optimized structure for tetracycline in its ground state is shown in Figure 1. Table 7 presents values of some quantum chemical parameters for tetracycline molecules. The frontier orbitals (highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important in defining the reactivity of a chemical species [52]. The energy of the HUMO (E_{HOMO}) is often associated with the electron donating ability of a molecule whereas the energy of the lowest unoccupied molecular orbital (E_{LUMO}) indicates the ability of a molecule to accept electron. Therefore, increasing values of E_{HOMO} and decreasing value of E_{LUMO} suggest efficient adsorption process. The calculated values of E_{HOMO} and E_{LUMO} obtained for tetracycline are comparable to values obtained for some adsorption inhibitors [27]. The energy gap ($E_{LUMO-HOMO}$) between the HOMO and the LUMO is another parameter that correlates with the reactivity of the molecules. Generally, the lower the energy gap, the better the electron transfer process. In this study, the energy gap for tetracycline is 0.1724 HF. This value is also comparable to values obtained for other inhibitors.

The total electronic energy and dipole moment for tetracycline were also found to be within the range of values reported for some inhibitors. The significant of these parameters is that decreasing value of dipole moment indicates efficient adsorption. From the values of total electronic energy, the ionization potential (IP) and electron affinity (EA) for tetracycline were calculated using the following equations [53].

$$IP = E_{(N-1)} - E_{(N)} \qquad (12)$$

$$EA = E_{(N)} - E_{(N+!)} \qquad (13)$$

where $E_{(N-1)}$, $E_{(N)}$ and $E_{(N+1)}$ are the ground state energies of the system with N-1, N and N+1 electrons respectively. Calculated values of IP and EA were -0.19285678 and 0.21203919 HF

respectively. Using the finite difference approximation, the global softness was evaluated as S = 1/(IP – EA) which transform to the following equation [54],

$$S = \frac{1}{[(E_{(N-1)} - E_{(N)}) - (E_{(N)} - E_{(N+!)})]} \tag{14}$$

Substituting the calculated values of IP and EA we obtained the value of -0.07040362 HF and 0.01918245 HF for the global softness and global hardness (which is the reciprocal of the global softness) respectively. From the results obtained, we noted that there are some similarities between the above parameters and frontier molecular energies. This is because ionization potential indicates the tendency of a molecule to donate electron while electron affinity is associated with the tendency of the molecule to accept electron. In this case, two systems, Fe (in mild steel) and inhibitor are brought together hence electron will flow from the lower system with lower electronegativity (inhibitor) to the system with higher electronegativity until the chemical potential becomes equal. The fraction of electron transferred, δ can be expressed as follows [33],

$$\delta = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \tag{15}$$

where χ_{Fe} and χ_{inh} are the electronegativity of the inhibitor and Fe respectively. $\chi = (IP + EA)/2$. η_{Fe} and η_{inh} are the global hardness of Fe and the inhibitor respectively. In order to validate equation 15 for this study, we use the theoretical value of $\chi_{Fe} = 7ev$ and $\eta_{Fe} = 0$ for the computation of δ. The results of our calculation indicates that $\delta = 0.389166$.

Table 7. Quantum chemical parameters of tetracycline.

Parameters	Values
E_{HOMO} (HF)	-0.3012
E_{LUMO} (HF)	-0.1289
Energy gap ($E_{LUMO-HOMO}$) (HF)	0.1724
Dipole moment (Debye)	6.70
Total energy (HF)	-214.74
Electronic energy (HF)	-2063.88
one electron energy (HF)	-9286. 42
Two electrons energy (HF)	4138.24
Nuclear repulsion energy (HF)	3602.69
Electron-electron potential energy (HF)	4138.24
Nuclear-electron potential energy (HF)	-10831.36
Nuclear-nuclear potential energy (HF)	3602.69
Total potential energy (HF)	-3090.42

Local reactivity

We used the Fukui function to analyze the local reactivity of tetracycline as an inhibitor for the corrosion of mild steel. The condensed Fukui functions and condensed local softness are parameters which enable us to distinguish each part of the molecule on the basis of its distinct chemical behavior due to different substituent functional groups. Stoyanov *et al.* [55-56], also stated that 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 $N + \delta$ electron system. The resulting change in electron density is the nucleophilic and electrophilic Fukui functions, which can be expressed using the finite difference approximation as follows,

$$f_x^+ \quad = \quad q_{(N+1)} - q_{(N)} \qquad\qquad (16)$$

$$f_x^- \quad = \quad q_{(N)} - q_{(N-1)} \qquad\qquad (17)$$

where $q_{(N+1)}$, $q_{(N)}$ and $q_{(N-1)}$ are the Mulliken charge of the atom with N+1, N and N-1 electrons. Table 8 present values of f_x^+ and f_x^- for tetracycline. As a rule, the respective site for electrophilic and nucleophilic attacks will be the place where the value of f_x^+ or f_x^- is maximum. From the results, it is evident that the site for nucleophilic attack in tetracycline is in hydroxyl bond (O23) because highest values of f_x^+ are found there. On the other hand, the sites for electrophilic attack are also in the hydroxyl bond (i.e O26).

The local softness, s_x for atom x is the product of the condensed Fukui function (f_x) and the global softness (S), as shown in equations 18 and 19.

$$S_x^+ \quad = \quad (f_x^+)S \qquad\qquad (18)$$

$$S_x^- \quad = \quad (f_x^-)S \qquad\qquad (19)$$

The local softness contains the same information as 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. The relative nucleophilicity and electrophilicity are defined as (sx+/sx-) and (sx-/sx+), respectively. From the results of the calculations presented in Table 8, it is also evident that data obtained for the global softness and the relative nucleophilicity /electrophilicity with respect to tetracycline also correlates with those obtained for the condensed Fukui functions. This also indicates that the hydroxyl atom (O26) has the tendency to donate electron.

Conclusions

From the results and findings of the study, the following conclusions are made,

(1) The results obtained from gravimetric, gasometric and thermometric methods indicate that tetracycline is a good inhibitor for the corrosion of mild steel in H_2SO_4. However, the average inhibition efficiency of tetracycline (obtained from gravimetric method) is better than its instantaneous inhibition efficiency (obtained from gasometric and thermometric methods).

(3) The occurrence of a physical adsorption mechanism for the adsorption of tetracycline on mild steel surface is supported by the pattern of variation of inhibition efficiency of tetracycline with temperature, range of values obtained for the activation and free energies. Furthermore, the adsorption of tetracycline on mild steel surface is spontaneous and endothermic.

(4) Synergistic combination of tetracycline with KCl and also with KBr, respectively improves the inhibition efficiency of tetracycline through enhanced adsorption.

(5) The inhibition action of tetracycline can be adequately explained using quantum chemical studies. The inhibitor acts via a donor-acceptor mechanism involving hydroxyl bonds.

Table 8. Local reactivity indices for carbon and electronegative atoms in tetracycline.

Atom No.	f_x^+	f_x^-	S_x^+	S_x^-	S_x^+/S_x^-	S_x^-/S_x^+
C(1)	4.2053	0.3205	-8.0563	-0.6140	13.1212	0.0762
C(2)	4.2360	0.3686	-8.1153	-0.7061	11.4928	0.0870
C(3)	3.9210	0.6722	-7.5118	-1.2878	5.8329	0.1714
C(4)	-4.2485	0.7499	8.1391	-1.4366	-5.6656	-0.1765
C(5)	-4.2262	0.9429	8.0965	-1.8063	-4.4823	-0.2231
C(6)	1.0119	0.5644	-1.9386	-1.0812	1.7930	0.5577
C(7)	-3.2024	-0.3445	6.1352	0.6601	9.2948	0.1076
C(8)	-4.6217	1.3508	8.8542	-2.5878	-3.4215	-0.2923
C(9)	-3.8832	0.2839	7.4393	-0.5438	-13.6798	-0.0731
C(10)	-3.6469	-0.3275	6.9866	0.6273	11.1370	0.0898
C(11)	-4.1921	0.0665	8.0312	-0.1275	-63.0024	-0.0159
C(12)	-3.4021	-1.0078	6.5178	1.9308	3.3757	0.2962
C(13)	-3.4862	0.3469	6.6788	-0.6646	-10.0488	-0.0995
C(14)	-0.5898	-1.3605	1.1299	2.6063	0.4335	2.3066
C(15)	3.4862	-1.6606	-6.6787	3.1813	-2.0993	-0.4763
C(16)	4.2062	-2.1798	-8.0582	4.1759	-1.9297	-0.5182
C(17)	-3.0703	0.0608	5.8821	-0.1166	-50.4608	-0.0198
C(18)	-1.3085	-0.0483	2.5068	0.0924	27.1182	0.0369
O(19)	4.6932	-1.5253	-8.9911	2.9222	-3.0768	-0.3250
O(20)	5.2569	-0.8460	-10.0710	1.6207	-6.2138	-0.1609
O(21)	5.5285	-2.4885	-10.5914	4.7674	-2.2216	-0.4501
C(22)	3.0741	0.3561	-5.8894	-0.6823	8.6320	0.1158
O(23)	-2.4612	1.6654	4.7151	-3.1905	-1.4778	-0.6767
O(24)	6.1948	0.2575	-11.8679	-0.4934	24.0531	0.0416
O(25)	2.0782	-0.1195	-3.9814	0.2289	-17.3922	-0.0575
O(26)	6.6116	-0.1758	-12.6664	0.3369	-37.6003	-0.0266
N(27)	-4.7684	1.3085	9.1352	-2.5069	-3.6440	-0.2744
C(28)	4.4439	-0.2980	-8.5135	0.5708	-14.9140	-0.0671
C(29)	1.2637	-0.1083	-2.4209	0.2075	-11.6685	-0.0857
C(30)	-1.1783	-0.3800	2.2573	0.7281	3.1004	0.3225
O(31)	-1.7175	0.6293	3.2904	-1.2057	-2.7291	-0.3664
N(32)	-3.7187	1.2539	7.1243	-2.4022	-2.9657	-0.3372

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