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Full Length Research Paper

Inhibition of the corrosion of mild steel in H_2SO_4 by 5-amino-1-cyclopropyl-7-[(3*R*, 5*S*) 3, 5-dimethylpiperazin-1-YL] -6, 8-difluoro-4-oxo-uinoline-3-carboxylic acid (ACPDQC)

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Adsorption and inhibitive efficiencies of ACPDQC on mild steel corrosion have been studied using gasometric and thermometric techniques. ACPDQC is found to be a good inhibitor for the corrosion of mild steel in H_2SO_4 solution. The inhibition efficiencies of ACPDQC were found to decrease with increase in temperature but increased with increase in the concentration of the extract. Thermodynamic/adsorption considerations revealed that the adsorption of ACPDQC on the surface of mild steel is exothermic, spontaneous and proceeded via the mechanism of physical adsorption. Classical adsorption isotherms of Langmuir and Frumkin best described the adsorption characteristics of ACPDQC on the surface of mild steel.

Key word: Corrosion, inhibition, ACPDQC.

INTRODUCTION

Mild steel is one of the most widely used metals in Industries. However, during industrial processes such as acid cleaning, prickling, etc, mild steel corrodes easily implying that the use of an inhibitor is necessary because the life of this valuable metal must be protected (Ebenso, 2003a, b). Due to their industrial applications, several inhibitors have either been synthesized or chosen from organic compounds having heteroatoms in their molecular structures (Abdallah, 2002). In addition, researches on the use of natural occurring substances have also been intensified (Okafor and Ebenso, 2007; Okafor et al., 2008, 2007; Oguzie et al., 2007; Onyeka et al., 2007; Rahendran et al., 2005). The latter class of inhibitors is preferred because they are environmentally friendly and are called green corrosion inhibitors (Eddy and Ebenso, 2008). Recently studies on the use of some drugs as corrosion inhibitors have been reported by some researchers. (Abdallah, 2004a, 2002; Eddy and Odoemelam, 2008a; Eddy and Ekop, 2008). Most of these drugs are heterocyclic compounds and were found to be environmentally friendly hence they have great potentials of competing with plant extracts. According to Eddy (2008), drugs are environmentally friendly because they do not contain heavy metals or other toxic compound. The present study seeks to investigate the adsorption and inhibitive properties of ACPDQC for the corrosion of mild steel. ACPDQC is a synthetic fluoroquinolone broad-spectrum antimicrobial agent in the same class as ofloxacin and norfloxacin. ACPDQC has in vitro activity against a wide range of gram-negative and gram-positive microorganisms. ACPDQC exerts its antibacterial activity by inhibiting DNA gyrase, a bacterial topoisomerase. DNA gyrase is an essential enzyme which controls DNA topology and assists in DNA replication, repair, deactivation, and transcription. Quinolones differ in chemical structure and mode of action from (beta)-lactam antibiotics. Quinolones may, therefore, be active against bacteria resistant to (beta)-lactam antibiotics. Although cross-resistance has been observed between ACPDQC and other fluoroquinolones, some microorganisms resis-

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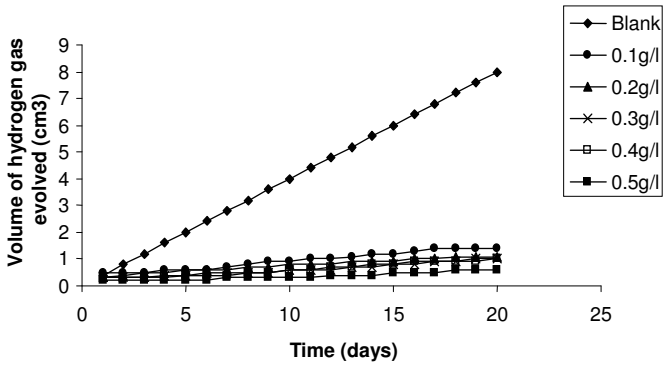


Figure 1. Variation of the volume of hydrogen gas evolved with time for the corrosion of the mild steel in 2.5 M tetraoxosulphate (VI) acid containing various concentrations of ACPDQC.

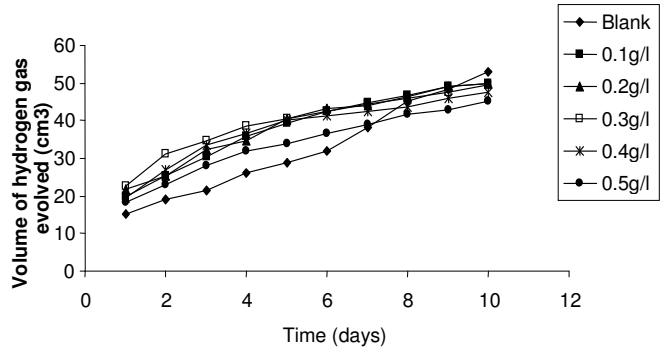
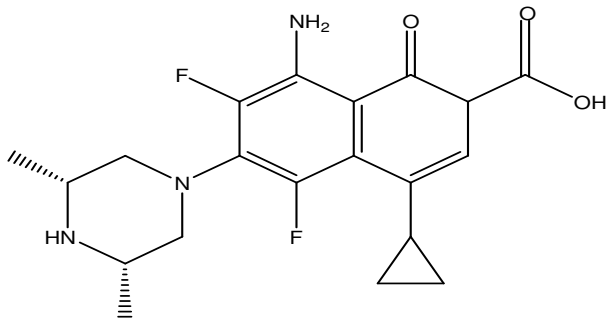


Figure 2. Variation of the volume of hydrogen gas evolved with time for the corrosion of mild steel in 2.5 M H_2SO_4 containing various concentrations of ACPDQC at 333 K.

resistant to other fluoroquinolones may be susceptible to ACPDQC. *In vitro* tests show that the combination of ACPDQC and rifampin is antagonistic against *Staphylococcus aureus*. The chemical structure of ACPDQC is shown below. Also structural properties of ACPDQC are also listed below the structure



Average molecular weight	=	392.3998
Monoisotopic molecular weight	=	392.1660
Experimental Water solubility	=	insoluble
Predicted water solubility	=	1.13×10^{-1} mg/L
Predicted logP/hydrophobicity	=	-0.06

Experimental

Materials used for the study were mild steel sheets with 5 x 4 x 0.11 cm dimensions which the chemical composition was (wt %) Mn (0.6), P (0.36), C (0.15) and Si (0.03). Each coupon was degreased in ethanol, dried in acetone and preserved in a desiccator before use. The inhibitor was supplied by LIVEMORE pharmaceutical company, Ikot Ekpene, Nigeria. All reagents used in this study were analar grade. Double distilled water was used for the preparation of all solutions. Concentrations of H_2SO_4 used for the study were 1.0, 1.5, 2.0 and 2.5 M while the concentrations of the inhibitor were 3.13×10^{-4}, 6.26×10^{-4}, 9.39×10^{-4}, 12.53×10^{-4} and 15.66×10^{-4} M which were dissolved in 2.5 M H_2SO_4.

Gasometric method

Hydrogen evolution measurements were carried out at 303 and 333 K as described in literature (Eddy and Ekop, 2008). From the volume of hydrogen evolved per minutes, inhibition efficiency (η), and degree of surface coverage (θ) were calculated using Equation 1 and 2 respectively.

$$\%I = \{1 - \frac{V'_{Ht}}{V^0_{Ht}}\} \times 100 \quad (1)$$

$$\theta = \%I/100 \quad (2)$$

Where V'_{Ht} is the volume of hydrogen evolved at time t for inhibited solution and V^0_{Ht} is the volume of hydrogen evolved at time t for inhibited solution.

Thermometric method

The thermometric tests were carried out as reported elsewhere (Eddy and Ebenso, 2008). From the rise in temperature of the system per minutes, the reaction number (RN) and inhibition efficiency were calculated using equation 3 and 4 respectively:

$$RN\ (^{\circ}C\ minutes^{-1}) = \frac{T_m - T_i}{t} \quad (3)$$

$$\%I = \frac{RN^0 - RN'}{RN} \times 100 \quad (4)$$

where T_m is the maximum temperature attained by the system, T_i is the Initial temperature, t is the time. RN^0 and RN' are the reaction numbers for the blank and inhibited solutions respectively.

RESULTS AND DISCUSSION

Figures 1 and 2 show the variation of the volume of hydrogen gas evolved with time for the corrosion of mild steel in 2.5 M H_2SO_4 solution containing various concentrations of ACPDQC at 303 and 333 K respectively. From the Figures, it was found that the volume of hydrogen gas evolved decrease with increase in the concentration of ACPDQC indicating that the corrosion rate of mild steel in 2.5 M H_2SO_4 is inhibited by ACPDQC. Comparing Figure 2 and 3, it was also found that the volume of hydrogen gas evolved also increase with increase in temperature indicating that the corrosion rate of mild steel increase

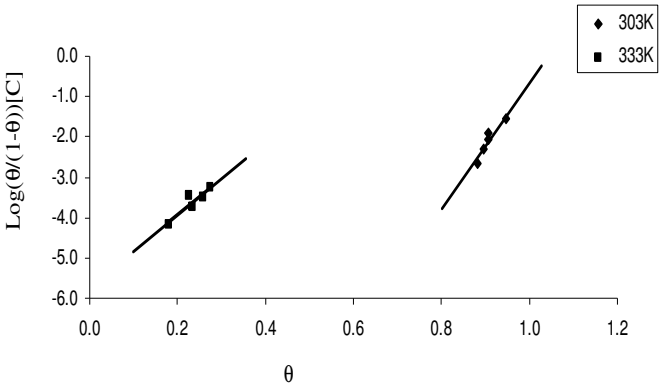


Figure 3. Frumkin isotherm for the adsorption of ACPDQC on the surface of mild steel.

Table 1. Corrosion rate (cm^3/minute) and reaction number (°C/minute) for the corrosion of mild steel in H_2SO_4 containing various concentration of ACPDQC.

Concentration (M)	CR(303K)	CR(333K)	RN(303K)
Blank	0.38	3.40	0.05
3.13×10^{-4}	0.05	2.99	0.04
6.26×10^{-4}	0.04	2.80	0.04
9.39×10^{-4}	0.04	2.71	0.03
12.53×10^{-4}	0.04	2.83	0.02
15.66×10^{-4}	0.02	2.65	0.02

with increase in temperature and that the inhibition efficiency of ACPDQC is reduced by increase in temperature.

Values of the corrosion rates (CR) and the reaction num-bers for the corrosion of mild steel in the presence of ACPDQC are presented in Table 1. From the results, it can be seen that the corrosion rate and reaction number of mild steel decreased with increase in the concentration of the inhibitor indicating that the inhibitor is an adsorption inhibitor (Eddy and Ebenso, 2008; Eddy and Odoemelam, 2008; Eddy and Ekop, 2008).

Table 2 shows values of inhibition efficiency of ACPDQC for the corrosion of mild steel. It can be seen from the Table that the inhibition efficiency of ACPDQC was reduced at higher temperature suggesting that the mechanism of adsorption of ACPDQC ion the surface of mild steel is physical adsorption (Ebenso, 2003a, b, 2004). The activation energy (E_a) for the corrosion of mild steel in the absence and presence of ACPDQC was calculated using Arrhenius theory. Assumptions of Arrhenius theory is expressed by Equation 5 (Umoren et al., 2008a, b).

$$CR = Aexp(-E_a/RT) \quad (5)$$

Where CR is the corrosion rate of mild steel, A is the

Table 2. Values of inhibition efficiency (%I) of ACPDQC for the corrosion of mild steel in H_2SO_4.

Concentration of ACPDQC (M)	Gasometric		Thermometric
	%I (303K)	%I (333K)	%I (303K)
3×10^{-4}	88.16	18.08	69.87
6×10^{-4}	89.47	23.29	69.87
9×10^{-4}	90.79	25.75	84.62
12×10^{-4}	90.79	22.47	89.75
15×10^{-4}	94.74	27.40	89.75

Arrhenius or pre-exponential factor, R is the gas constant and T is the temperature. Taking the logarithm of both sides of Equation 5, Equation 6 is obtained,

$$\log (CR_2/CR_1) = E_a/2.303R\ (1/T_1 - 1/T_2) \quad (6)$$

Where CR1 and CR2 are the corrosion rates at the temperatures T1 (303 K) and T2 (333 K) respectively

Values of corrosion rate recorded in Table 1, have been used to calculate the values of activation energy for the corrosion of mild steel in the absence and presence of ACPDQC. These values were higher than the value (36 J/mol) obtained for the blank and tend to increase with increase in the concentration of the inhibitor indicating that there is an increasing ease of adsorption of the inhibitor with increasing concentration. Also the activation energy were found to be lower than the threshold value of 80 KJ/mol required for chemical adsorption indicating that a physical adsorption mechanism is applicable to the adsorption of ACPDQC on the surface of mild steel (Ebenso, 2003a, b).

The heat of adsorption (Q_{ads}) of ACPDQC on the surface of mild steel was calculated using Equation 7 (Eddy and Ebenso, 2008; Eddy and Odoemelm, 2008a, b),

$$Q_{ads} = 2.303\ R[\log(\theta_2/1-\theta_2) - \log(\theta_1/1-\theta_1) \times (T_2T_1)/(T_2 - T_1) \quad (7)$$

where R is the gas constant, θ_1 and θ_2 are the degree of surface coverage at temperatures, T_1 and T_2 respectively. Values of Q_{ads} calculated from Equation 7 ranged from are recorded in Table 3. These values are negative indicating that the adsorption of ACPDQC on mild steel surface is exothermic.

Adsorption isotherms were used to investigate the mode of adsorption and the adsorption characteristics of ACPDQC on mild steel surface (Abdallah, 2004a, b; Oguzie et al., 2007). The values of degree of surface coverage were calculated for different concentration of ACPDQC and used to fit curves for different adsorption isotherms. The results revealed that Langmuir, Frumkin and Freundlich adsorption isotherms are the best isotherms that described the adsorption characteristics of

Table 3. Some thermodynamic parameters for the adsorption of ACPDQC on mild steel surface.

Concentration of ACPDQC (M)	E_a (J/mol)	Q_{ads} (J/mol)
3.13×10^{-4}	69.79	-186.1528
6.26×10^{-4}	70.66	-176.309
9.39×10^{-4}	72.33	-177.093
12.53×10^{-4}	73.05	-186.611
15.66×10^{-4}	79.26	-204.496

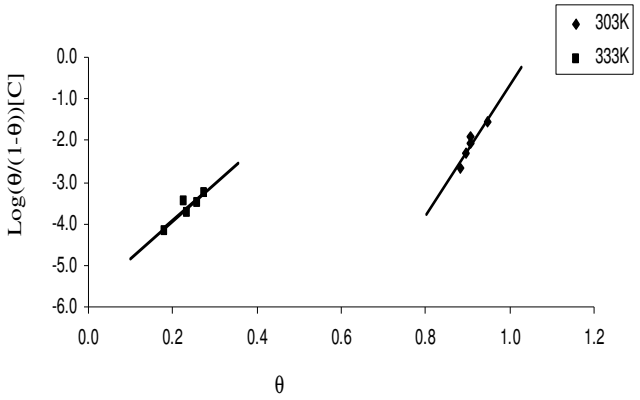


Figure 3. Frumkin isotherm for the adsorption of ACPDQC on the surface of mild steel.

ACPDQC on mild steel surface.

Frumkin adsorption isotherm can be expressed according to Equation 8,

$$\log \{[C] *(\theta/ (1-\theta)\} = 2.303 \log K + 2\alpha\theta \quad (8)$$

Where K is the adsorption-desorption equilibrium constant and α is the lateral interaction term describing the molecular interaction in adsorbed layer (Bilgic and Caliskan, 1999). Figure 3 shows Frumkin adsorption plots for the adsorption of ACPDQC on the surface of mild steel. Values of Frumkin adsorption parameters deduced from the plots are recorded In Table 4. From the results, values of α were found to be positive indicating the attractive behaviour of ACPDQC on the surface of mild steel (Ashassi-Sorkhabi et al., 2005).

Langmuir adsorption isotherm is the ideal adsorption isotherm for physical and chemical adsorption on a smooth surface where there is no interaction between adsorbed molecules and the surface (Eddy and Ebenso, 2008). If it is assumed that adsorption of ACPDQC on mild steel surface proceeded according to Langmuir adsorption, then Equation 8 is applicable (Ehteshamzade et al., 2006):

$$C/\theta = 1/k + C \quad (9)$$

Where k is the equilibrium constant of adsorption. Taking the logarithm of both sides of Equation 9, Equation 10 is obtained:

$$\log(C/\theta) = \log C - \log K \quad (10)$$

From Equation 10, a plot of $\log(C/\theta)$ versus logC should give a straight line with intercept equals to -logK (Ashassin-Sorkhabi et al., 2006). Figure 4 shows Langmuir plot for the adsorption of ACPDQC on mild steel surface. The application of Langmuir isotherm to the adsorption of ACPDQC on the surface mild steel indicates that the addition of ACPDQC causes a high increase in the free energy with respect to the uninhibited system (Asahassi-Sorkhabi et al., 2006). The adsorption parameters deduced from Langmuir adsorption isotherm are also presented in Table 4.

The free energy of adsorption (ΔG_{ads}) of ACPDQC on mild steel surface is related to the equilibrium constant of adsorption according to Equation 11 (Ashassi-Sorkhabi et al., 2006; Bailgic and Caliskan, 1999; Ebenso, 2003a, b).

$$\Delta G_{ads} = -2.303RT \log(55.5K) \quad (11)$$

Where T is the temperature and K is the equilibrium constant of adsorption. Free energy data calculated from values of K obtained from Frumkin, Langmuir and Freundlich isotherms were given in Table 4. From the results, average values of ΔG_{ads} were found to be negative and were below the threshold value of -40 KJ/mol indicating that the adsorption of ACPDQC on mild steel surface is spontaneous and that the mechanism of physical adsorption is applicable (Eddy and Ekop, 2008).

From the chemical structure of ACPDQC, it can be seen that ACPDQC contain a heteroatom (nitrogen) in its cyclic structure. The presence of this atom and the electronegative fluorine atom in ACPDQC might have enhanced the electron donating ability of this compound hence its inhibition efficiency. Also, the functional groups (-C=O, -NH_2 and –COOH) presence in ACPDQC might have provided sites for the adsorption of the inhibitor on the surface of mild steel. We therefore proposed the following schemes for the mechanism of adsorption of ACPDQC on the surface of mild steel.

i.) In acidic medium, ACPDQC undergoes hydrolysis to form structure b. Each molecule of structure b can donate electron to vacant d-orbital of iron and formed a coordinate covalent bond (structure c) (Figure 5: Scheme 1).

ii.) Another mechanism is shown by scheme 2 (Figure 6). In this scheme, the electron donated for the formation of Fe-ACPDQC complex is provided by the carboxylic acid functional group instead of the carbonyl group as shown by Scheme 2.

iii.) In scheme 3 (Figure 7), both carbonyl and carboxylic acid functional groups are involved in the formation of bond between Fe (in mild steel) and ACPDQC.

Table 4. Values of Langmuir, Frumkin and Freundlich adsorption parameters.

	Temperature (K)	Slope	logK	R^2	ΔG_{ads} (KJ/mol)
Langmuir	303	2.6281	2.6703	0.9784	-3.7414
	333	2.3035	1.5525	0.999	-3.3033
	Temperature (K)	**α**	**logK**	**R^2**	**ΔG_{ads} (KJ/mol)**
Frumkin	303	0.2228	1.4935	0.8913	-2.9603
	333	0.1965	1.5079	0.9803	-3.2656

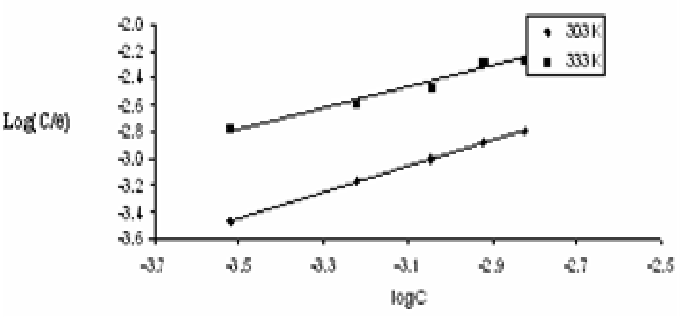


Figure 4. Langmuir isotherm for the adsorption of ACPDQC on the surface of mild steel.

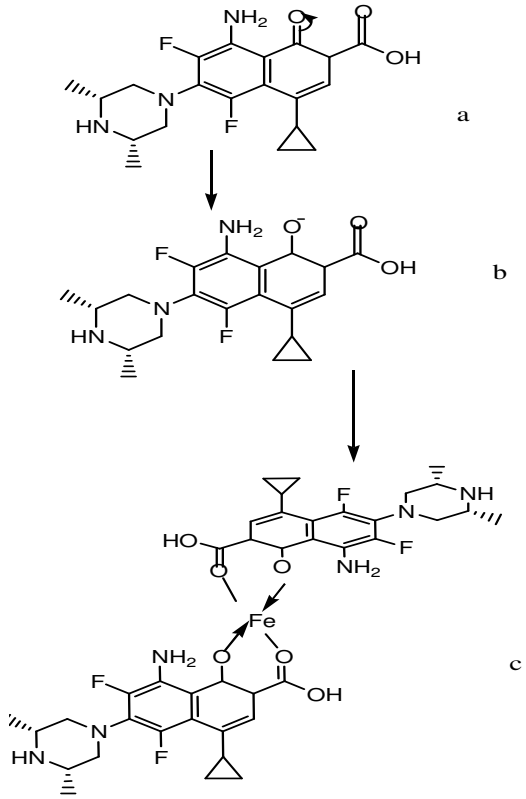


Figure 5. Scheme 1, mechanism of adsorption of ACPCQC on the surface of mild steel.

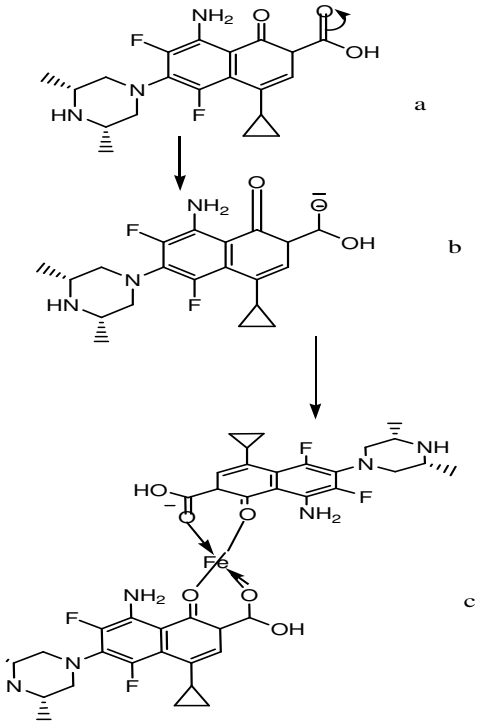


Figure 6. Scheme 2 mechanism of adsorption of an ACPDQC on the surface of mild steel.

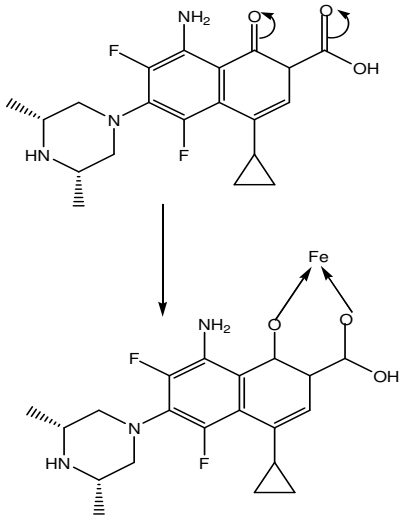


Figure 7. Scheme 3, mechanism of adsorption of ACPDQC on the surface of mild steel.

Conclusion

From the study, we have found that the corrosion of mild steel in H_2SO_4 depends on the concentrations of the acid/inhibitor, temperature and the period of contact. ACPDQC inhibited the corrosion of mild steel through physical adsorption. The adsorption of ACPDQC on mild steel surface is spontaneous, exothermic and is consistent with the models of Langmuir, and Frumkin isotherms. ACPDQC is hereby recommended as a good inhibitor for the corrosion of mild steel.

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