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Full Length Research Paper

Inhibition of the corrosion of mild steel in H_2SO_4 by penicillin G

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Inhibitive and adsorption properties of penicillin G for the corrosion of mild steel was investigated using gasometric and thermometric methods. Penicillin G is found to inhibit the corrosion of mild steel in H_2SO4. Inhibition efficiencies of penicillin G increased as the concentration of penicillin G increases but decreased with increase in temperature. Penicillin G is found to act as an adsorption inhibitor for the corrosion of mild steel. The adsorption of the inhibitor on the surface of mild steel was found to be exothermic, spontaneous and followed the mechanism of physical adsorption. Also Langmuir adsorption isotherm was found to be the best isotherm that described the adsorption characteristics of the inhibitor.

Key word: Corrosion of mild steel, inhibition, penicillin G.

INTRODUCTION

Protection of metals against corrosion is a major Industrial problem that has attracted numerous re-searches (Abiola et al., 2004, 2005; Agrawal et al., 2003; Arora et al., 2007; Ashassi-Sorkhabi and Ghalebzaza, 2005; Ashassi-Sorkhabi et al., 2005a,b,c,2004). Corro-sion inhibitors are chemicals that react with a metallic surface, or the environments the metal surface is expo-sed to and act to protect the metal against corrosion (Eddy and Odoemelam, 2008a, b; Emregul et al., 2006a, b, 2005a, b).

Most organic compounds having heteroatom(s) (N, S, O, P) in their aromatic or long carbon chain have been successfully used as corrosion inhibitors (Aytac et al., 2005; Babi-Samardzija et al., 2005). These compounds contain electron rich bond that facilitates the formation of a protective layer. Some naturally occurring compounds such as ethanol or methanol extract of plants have also been found to be good corrosion inhibitors due to the presence of tannin, saponin and other phytochemical constituents (Ogundipe et al., 2003; Oguzie, 2006a-c, 2005; Oguzie et al., 2007, 2006, 2004a-c; Okafor et al., 2008, 2007a,b;2005). Recently, the use of antibiotics and other drugs have been investigated and their inhibition efficiencies have been linked with their heterocyclic nature (Abdallah, 2004a,b; Eddy and Odoemelam, 2008a,b; Eddy and Ekop, 2008). The unique advantage of using natural products for the inhibition of the corrosion of metals is that they are environmentally friendly. Similarly, Eddy and Odoemelam (2008a) stated that most heterocyclic drugs are environmentally friendly and can favourably compete with the natural products. However, studies on the use of drugs as corrosion inhibitors are scanty. The present study aims to investigate inhibitive properties of penicillin G for the corrosion of mild steel. Penicillin G is chemically designated as 4-thia-1-azabicyclo [3,1,0] heptane-2-carboxylic acid, 3,3-dimethyl-7-oxo-6-[(phenylacetyl)amino]-, monopotassium salt,[2s-(2,5,6] (Figure 1).

EXPERIMENTAL

Materials used for the study were mild steel sheets of composition (wt, %) Mn (0.6), P (0.36), C (0.15), Si (0.03) and dimension, 5 x 4 x 0.11 cm. Each coupon was degreased by washing in ethanol, dried in acetone and preserved in a desiccator. The inhibitor was supplied by VERBATA pharmaceutical store, Ikot Ekpene, Nigeria.

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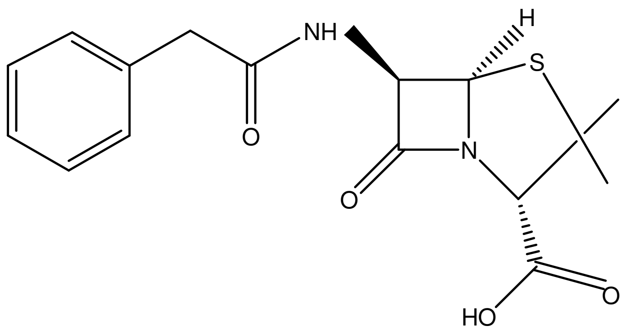

Figure 1. Structure of penicillin G.

Table 1. Values of corrosion rate (cm^3/min) and reaction number (°C/min) for the corrosion of mild steel in H_2SO_4.

Conc. of H_2SO_4 (M)	CR (303 K)	RN (303 K)
1.0	0.175	0.0167
1.5	0.180	0.0200
2.0	0.220	0.0267
2.5	0.380	0.0500

All reagents used for the 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 x 10^{-4}, 6 x 10^{-4}, 9 x 10^{-4}, 12 x 10^{-4} and 15 x 10^{-4} M. These were respectively 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 (%I), and degree of surface coverage (θ) were calculated using equations 1 and 2, respectively:

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

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

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 uninhibited solution.

Thermometric method

This was also carried out as reported elsewhere (Eddy and Ebenso, 2008). From the rise in temperature of the system per minute, the reaction number (RN) and inhibition efficiency were calculated using equations 3 and 4 respectively:

$$RN\ (°C\ min) = (T_m - T_i) / t \quad (3)$$

$$\%I = [(RN_b - RN_w)/ RN_b] \times 100 \quad (4)$$

Where T_m and T_i are the maximum and the minimum temperatures attained by the system at time, t. RN_b and RN_w are the reaction numbers for the uninhibited and inhibited systems, respectively.

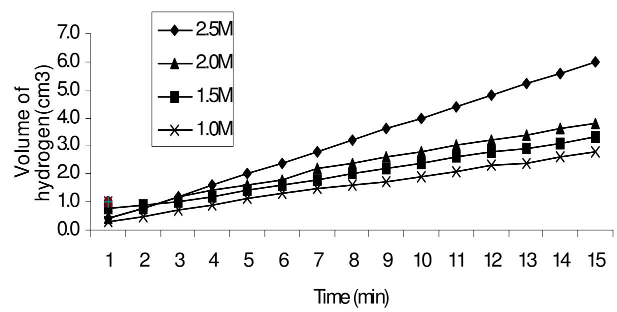

Figure 2. Variation of hydrogen gas evolved with time for the corrosion of mild steel at various concentrations of teraoxosulphate (V1) at 303 K..

RESULTS AND DISCUSSION

Figure 2 shows the variation of volume of hydrogen gas evolved with time during the corrosion of mild steel in various concentrations of H_2SO_4. The Figure revealed that the rate of corrosion of mild steel in H2SO4 increased with increase in the concentration of the acid. Values of reaction number (RN) and corrosion rate (CR) of mild steel in various concentrations of H2SO4 are recorded in Table 1. The results indicated that the CR and RN increased with increased in the concentration of the acid indicating that the rate of corrosion of mild steel in H2SO4 increased as the concentration of the acid increases.

Figures 3 and 4 show the variation of the volume of hydrogen gas evolved for the corrosion of mild steel in 2.5M H_2SO_4 containing various concentrations of penicillin G at 303 and 333 K respectively. The figures revealed that the rate of corrosion of mild steel increased with increase in temperature and with the period of contact. The figures also revealed that the rate of hydrogen gas evolution in the presence of various concentrations of penicillin G were lower than the corresponding rate for the blank indicating that penicillin G inhibited the corrosion of mild steel in H_2SO_4. The corrosion rates and reaction numbers of mild steel in 2.5 M H2SO4 containing various concentrations of penicillin G are recorded in Table 2. The values of inhibition efficiency of penicillin G for the corrosion of mild steel are also recorded in the same Table. From the results, it can be seen that the inhibition efficiency of penicillin G increased as the corrosion rates decrease indicating that penicillin retarded the rate of corrosion of mild steel in H2SO4 (Gomma and Whadan, 1995).

In order to study the effect of temperature on the corrosion of mild steel in the absence and presence of various concentration of penicillin G, the Arrhenius equation (Equation 5) was used:

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

Table 2. Corrosion rate, reaction number of mild steel in H2SO4 (containing penicillin G) and inhibition efficiency of penicillin G for the corrosion of mild steel in H2SO4.

Penicillin G (M)	CR (303K)	CR (333K)	RN (303K)	Gasometric		Thermometric
				%I (303 K)	%I (333 K)	%I (303 K)
3×10^{-4}	0.238	2.292	0.030	36.67	1.64	40.23
6×10^{-4}	0.188	2.231	0.025	50.00	9.13	50.00
9×10^{-4}	0.131	1.500	0.025	65.00	23.89	50.00
12×10^{-4}	0.119	1.337	0.017	68.33	28.81	65.43
15×10^{-4}	0.038	1.323	0.013	90.00	29.27	73.68

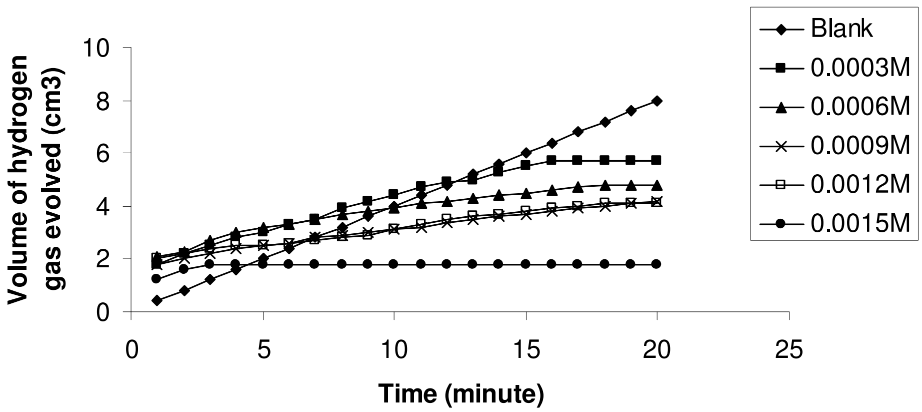

Figure 3. Variation of the volume of hydrogen gas evolved with time for the inhibition of the corrosion of mild steel by various concentrations of pencillin G at 303 K.

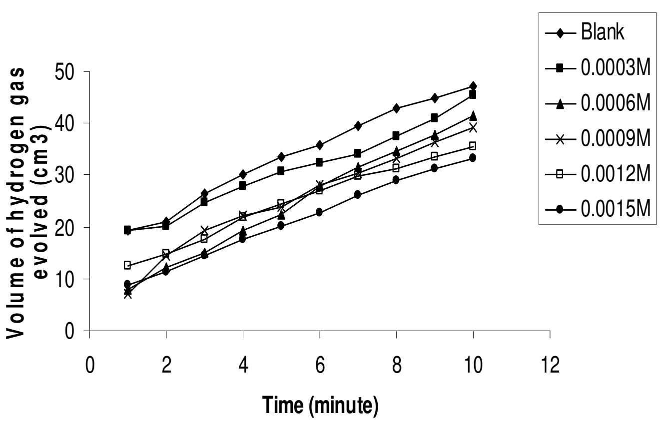

Figure 4. Variation of the volume of hydrogen gas evolved with time for the inhibition of the corrosion of mild steel by various concentrations of pencillin G at 333 K.

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

activation energy, R is the gas constant and T is the temperature. Taking the logarithm of both sides of equation 5, equation 6 is obtained:

$$\log CR = \log A - E_a/2.303RT \quad (6)$$

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

Penicillin G (M)	E_a (J/mol)	Q_{ads}(KJ/mol)
3×10^{-4}	63.48	-74.41
6×10^{-4}	69.34	-48.20
9×10^{-4}	68.20	-37.29
12×10^{-4}	67.78	-35.11
15×10^{-4}	99.77	-64.60
Blank	55.67	

Assuming that at temperature T_1, the corrosion rate of mild steel is CR_1 and at another temperature, T_2, the corrosion rate changes to CR_2 (where $T_2>T_1$), then equation 6 can be expressed as follows::

$$\log CR_1 = \log A - E_a/2.303RT_1 \quad (7)$$

$$\log CR_2 = \log A - E_a/2.303RT_2 \quad (8)$$

Dividing Equation 8 by equation 7, equation 9 is obtained:

$$\log(CR_2/CR_1) = E_a/2.303R(1/T_1 - 1/T_2) \quad (9)$$

Values of E_a calculated from equation 9 are recorded in Table 3. The value for the blank was 55.667 J/mol. In

Table 4. Values of Langmuir adsorption parameters.

Temperature (K)	Slope	logK	R^2	ΔG_{ads} (KJ/mol)
303	0.4732	-0.0807	0.9618	-9.6515
333	0.6082	0.0638	0.9327	-10.4898

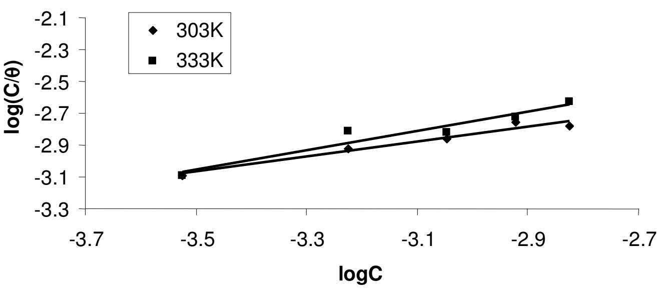

Figure 5. Langmuir isotherm for the adsorption of pencillin G on the steel surface.

the presence of penicillin G, E_a values ranged from From the results, the activation energies for the corrosion of mild steel in the presence of penicillin G are less than the threshold value of 80KJ/mol required for chemical adsorption indicating that the adsorption of penicillin G on the surface of mild steel is consistent with the mechanism of physical adsorption. (Ebenso, 2003a,b, 2004; Sheatty et al., 2006). The significant difference between these values and the value for the blank ($P \geq 0.05$) indicate that penicillin G retards the corrosion of mild steel in H_2SO_4 (Eddy and Ebenso, 2008).

Values of the heat of adsorption of penicillin G on mild steel surface were calculated using equation 10 (Umoren et al., 2006a-c).

$$Q_{ads} = 2.303R[\log(\theta_2/1-\theta_2) - \log(\theta_1/1-\theta_1) \times (T_2T_1)/(T_2 - T_1)] \quad (10)$$

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. Calculated values of Q_{ads} were negative and ranged from -35.1050 to -74.4119 KJ/mol, indicating that the inhibited corrosion of mild steel is exothermic.

Values of degree of surface coverage calculated through equation 2 were used to fit curves for different adsorption isotherms including Langmuir, Frumkin, Temkin, El awardy et al. Bockris–Swinkle, Freundlich and Flory–Huggins adsorption isotherms (Eddy and Odoemelam, 2008a,b; Umoren et al., 2006a-d). The isotherms that best described the adsorption characterristics of penicillin G is Langmuir adsorption isotherm.

Suppose the assumptions of Langmuir isotherm are valid for the inhibition of the corrosion of mild steel by penicillin G, then equation 11 is applicable.

$$\theta = bC/(1+bC) \quad (11)$$

where θ is the degree of surface coverage, k is the equilibrium constant of adsorption and C is the bulk concentration of the inhibitor in the electrolyte. Rearranging equation 11, equations 12 and 13 are obtained:

$$\theta + \theta kC = kC \quad (12)$$

$$C/\theta = 1/k + C \quad (13)$$

Taking the logarithm of both sides of equation 13, equation 14 is obtained:

$$\mathrm{Log}(C/\theta) = \log C - \log k \quad (14)$$

From equation 14, a plot of log(C/θ) versus logC should give a straight line if the assumptions of Langmuir are valid. Figure 5 shows Langmuir adsorption isotherm for the adsorption of penicillin G on the surface of mild steel. Values of Langmuir adsorption parameters are recorded in Table 4.

The equilibrium constant of adsorption (k) is related to the free energy of adsorption according to equation 15 (Asshassi-Sorkhabi et al., 2006; Ebenso, 2004; Ehteshanmzade et al., 2005).

$$\Delta G_{ads} = -2.303RT\log(55.5k) \quad (15)$$

The values of K calculated from the slopes of Langmuir adsorption isotherm were used to compute values of free energy of adsorption. These values are recorded in Table 4. The values are negative and less than threshold value (-40 KJ/mol) required for physical adsorption indicating that adsorption of penicillin G on mild steel surface is spontaneous and occurred according to the mechanism of physical adsorption.

The molecular structure of penicillin G shows that it contains hetero atoms (N, S) which enhance its inhibition efficiency. In acidic medium, penicillin G can be hydrolysed and produce anhydrous penicillin G (Figure 6a). This compound contains free electron which can be donated to vacant d-orbital of Fe in mild steel leading to the formation of a complex that protects the metal against corrosion (Figure 6b).

Conclusion

Penicillin G is a good inhibitor for the corrosion of mild steel. Penicillin G is an adsorption inhibitor and its inhibition behaviour follows the Langmuir adsorption isotherms. Adsorption of the inhibitor on mild steel surface is exothermic and spontaneous. Inhibition efficiency of peni-

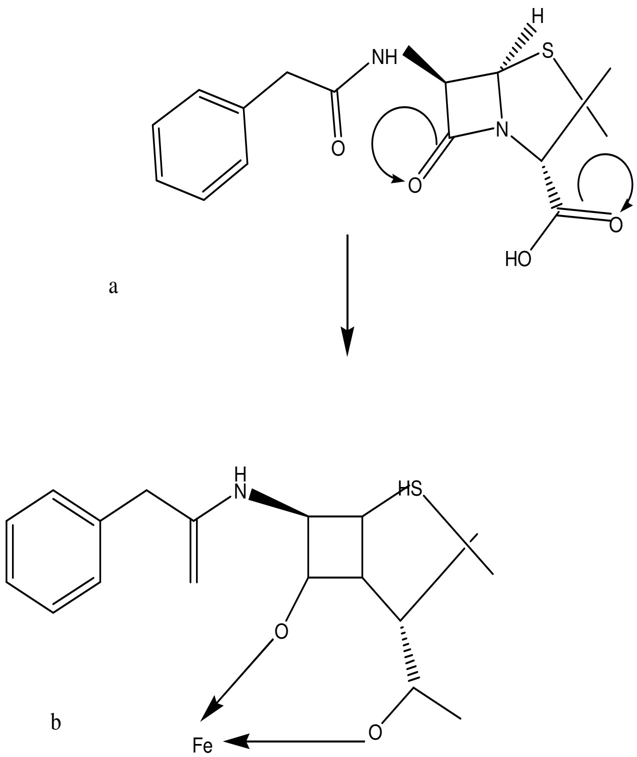

Figure 6. Formation of Fe-pencillin complex.

penicillin G for mild steel corrosion shows a decrease with increase in temperature therefore a physical adsorption mechanism is proposed at 3 x 10^{-4} to 12 x 10^{-4} M but at higher concentration (15 x 10^{-4} M) chemical adsorption is obeyed within the concentration range studied.

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