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Adsorption and Inhibitive Properties of Clarithromycin for the Corrosion of Zn in 0.01 to 0.05 M H_2SO_4

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Abstract

The corrosion of zinc in 0.01 to 0.04 M H_2SO_4 was studied using gravimetric and gasometric methods of monitoring corrosion. The results obtained indicate that clarithromycin is a good adsorption inhibitor for the corrosion of zinc in H_2SO_4. The inhibition efficiency of clarithromycin increases with increasing concentration but decreases with increasing temperature. There was no significant difference between the inhibition efficiencies of clarithromycin obtained at various concentrations of H_2SO_4 ($P>0.5$), but values of inhibition efficiency tend to decrease with increasing concentration of the acid. The adsorption of clarithromycin on zinc surface is endothermic, spontaneous and is best described by Langmuir adsorption isotherm. Calculated values of activation energies and free energies of adsorption indicate that the adsorption of clarithromycin on zinc surface supports the mechanism of physical adsorption.

Keywords: corrosion, inhibition, clarithromycin.

Introduction

Corrosion of metals is usually accelerated by aggressive solutions such as acidic, alkaline and salt solutions. Contacts between most of the valuable metals (such as zinc, mild steel and aluminium) can not be avoided because of their industrial significance, implying that the use of inhibitors is necessary [1-5]. It has been established that the initial step in any corrosion inhibition process is the adsorption of the inhibitor on the surface of the metal [6].

Several inhibitors, including, quinoline, aniline, ephedrine, narcotine, brucine, stryctuine, piperazine, caffine, barbitone, sparfloxacin, norfloxacin, azithromycin and pyridine derivatives have been investigated as corrosion inhibitors for zinc

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[7-19]. A close examination of these inhibitors reveals that they are organic compounds having one or more hetero atoms (N, O, S or P) in their aromatic/long carbon chain system. For this class of inhibitors, the presence of hetero atoms enhances the adsorption of the inhibitor on the surface of the metal [20-23]. In spite of the broad spectrum of inhibitors, synthesised and used for the inhibition of zinc corrosion, a search for eco-friendly inhibitors has provoked enormous researches. Environmental friendly inhibitors (green inhibitors) are often gotten from extract of naturally occurring compounds such as ethanol extract of some plants [24-30]. On the context of inhibition, most plant extracts have proven to be suitable as green corrosion inhibitors. Also, in our research group, we have explored the potentials behind some drugs as green corrosion inhibitors for the corrosion of metals. On this list are sparfloxacin, norfloxacin, ampicillin, tetracycline, nitrofurantin, amoxicillin, azithromycin, tetracycline, chloramphenicle, ofloxacin, ciprofloxacin, methocarbamol, etc. [31-38]. In all these and other studies, clarithromycin has not been reported as an inhibitor for the corrosion of zinc in H_2SO_4. Therefore, the objective of the present study is to investigate the adsorption and inhibitive properties of clarithromycin for the corrosion of zinc in H_2SO_4.

Clarithromycin is a broad spectrum antibiotic which belongs to the family of the microlides The IUPAC name of clarithromycin is (3*R*,4*S*,5*S*,6*R*,7*R*,9*R*,11*S*,12*R*, 13*S*,14*S*)-6-{[(2*S*,3*R*,4*S*,6*R*)-4-dimethylamino)-3-hydroxy-6-methyloxan-2-yl] oxy}-14-ethyl-12,13-dihydroxy-4-[(2*R*,4*S*,5*S*,6*S*)-5-hydroxy-4-methoxy-4,6-di-methyloxan-2-yl]oxy}-7 -methoxy-3,5,7,9,11,13-hexamethyl -1-oxacyclotetrade-cane-2,10-dione. The compound has a molar mass of 747.957 g/mol, molecular formula of $C_{38}H_{69}NO_{13}$ and its structural formula is as shown in Fig. 1.

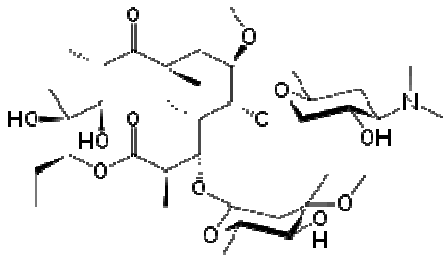

Figure 1. Chemical structure of clarithromycin.

From the above chemical structure, it can be seen that clarithromycin has some functional groups and hetero-atom (oxygen) in its structure hence it is expected to be a good inhibitor for the corrosion of zinc.

Experimental details

Materials

The material used for the study was zinc sheet of composition (w/%); Pb (0.001), Fe (0.002), Cd (0.001), Cu (0.003) and the rest, zinc. The sample was mechanically pressed cut into different coupons, each of dimension, 5x4x0.11 cm. Each coupon was degreased by washing with ethanol, dipped in acetone and

allowed to dry in air before it was preserved in a desiccator. All reagents used for the study were Analar grade and double distilled water was used for their preparation.
The inhibitor (clarithromycin) was supplied by LIVEMOORE Pharmaceutical Company, Ikot Ekpene, Akwa Ibom State, Nigeria, and was used without further purification. The concentration range used for the inhibitor (clarithromycin) was 0.0001 to 0.0005 M.

Gravimetric method

In the weight loss experiment, the pre-cleaned zinc coupon was dipped in 200 mL of the test solution maintained at 303 K in a thermostated bath. The weight loss was determined by retrieving the coupons at 24 h interval progressively for 168 h (7 days). Prior to measurement, each coupon was washed in 5% chromic acid solution (containing 1% silver nitrate) and rinsed in deionized water. The difference in weight was taken as the weight loss of zinc. The experiments were also carried at 313 and 323 K, as described above.
From the weight loss measurements, the inhibition efficiency (%I) of the inhibitor, degree of surface coverage (θ) and the corrosion rate (CR) of zinc were calculated using equations 1, 2 and 3, respectively [39].

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

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

$$CR = W/At \quad (3)$$

where W_1 and W_2 are the weight losses (in g) for zinc 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 zinc coupon (in cm^2), t is the period of immersion (in hours), W is the weight loss of zinc steel after time t, and CR is the corrosion rate of zinc in $gh^{-1}cm^{-2}$.

Gasometric method

Gasometric experiments were carried out at 303 K as described in the literature [39]. From the volume of hydrogen evolved per minute, inhibition efficiencies were calculated using equation 4,

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

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.

Table 1. Corrosion rates (in gcm^{-2} h^{-1}) of zinc and inhibition efficiencies (%) of clarithromycin (clar) in various concentrations of H_2SO_4.

Systems	Corrosion rate x 10^2			Inhibition efficiency (%)		
	303	313	323	303	313	323
0.01 M H_2SO_4	3.78	3.87	4.08	-	-	-
1 x 10^{-4} M Clar + 0.01 M H_2SO_4	0.93	1.52	1.96	75.58	60.77	51.82
2 x 10^{-4} M Clar + 0.01 M H_2SO_4	0.89	1.43	1.70	76.38	63.08	58.39
3 x 10^{-4} M Clar + 0.01 M H_2SO_4	0.88	1.25	1.49	78.73	67.69	63.50
4 x 10^{-4} M Clar + 0.01 M H_2SO_4	0.77	1.22	1.43	79.52	68.46	64.96
5 x 10^{-4} M Clar + 0.01 M H_2SO_4	0.71	1.19	1.34	81.11	69.23	67.15
0.02 M H_2SO_4	4.17	4.43	4.61	-	-	-
1 x 10^{-4} M Clar + 0.02 M H_2SO_4	1.52	1.61	2.17	63.57	63.76	52.90
2 x 10^{-4} M Clar + 0.02 M H_2SO_4	1.43	1.49	1.76	65.71	66.44	61.94
3 x 10^{-4} M Clar + 0.02 M H_2SO_4	1.25	1.40	1.70	70.00	68.46	63.23
4 x 10^{-4} M Clar + 0.02 M H_2SO_4	1.12	1.37	1.64	75.71	69.13	64.52
5 x 10^{-4} M Clar + 0.02 M H_2SO_4	0.77	1.25	1.49	81.43	71.81	67.74
0.03 M H_2SO_4	4.32	4.64	4.94	-	-	-
1 x 10^{-4} M Clar + 0.03 M H_2SO_4	1.88	2.98	3.27	56.55	35.90	33.73
2 x 10^{-4} M Clar + 0.03 M H_2SO_4	1.64	2.86	3.10	62.07	38.46	37.35
3 x 10^{-4} M Clar + 0.03 M H_2SO_4	1.40	2.59	2.80	67.59	44.23	43.37
4 x 10^{-4} M Clar + 0.03 M H_2SO_4	1.22	2.38	2.62	71.72	48.72	46.99
5 x 10^{-4} M Clar + 0.03 M H_2SO_4	1.01	1.96	2.23	76.55	57.69	54.82
0.04 M H_2SO_4	5.15	6.55	6.88	-	-	-
1 x 10^{-4} M Clar + 0.04 M H_2SO_4	1.96	3.13	3.57	61.85	46.97	45.45
2 x 10^{-4} M Clar + 0.04 M H_2SO_4	1.70	2.98	3.36	67.05	49.49	48.64
3 x 10^{-4} M Clar + 0.04 M H_2SO_4	1.64	2.92	3.27	68.21	50.51	50.00
4 x 10^{-4} M Clar + 0.04 M H_2SO_4	1.58	2.62	2.86	69.36	55.56	56.36
5 x 10^{-4} M Clar + 0.04 M H_2SO_4	1.43	2.20	2.38	72.25	62.63	63.64

Results and discussion

Effect of concentration of clarithromycin/H_2SO_4 on zinc corrosion

Figs. 2a to 2c show the variation of weight loss with time for the corrosion of zinc in 0.01 M H_2SO_4 (containing various concentrations of clarithromycin) at 303, 313 and 323 K, respectively. It is evident from Figs. 2a to 2c that weight losses of zinc for the blank solutions are higher than those obtained for solutions containing various concentrations of clarithromycin. The plots also indicate that weight loss of zinc decreases with increasing concentration of clarithromycin, but increases with increasing temperature. These also imply that the rate of corrosion of zinc in H_2SO_4 is retarded by clarithromycin and that the inhibition efficiency of clarithromycin increases with increasing concentration, but decreases with increasing temperature. At higher concentration of H_2SO_4, weight losses of zinc were also found to be higher, indicating that the corrosion rates of zinc in H_2SO_4

(in the absence and presence of various concentrations of clarithromycin) also increase with increasing concentration of H_2SO_4. Conversely, the inhibition efficiency of clarithromycin is expected to decrease with increasing concentration of H_2SO_4 and our results (Table 1) support this assertion. A close examination of the results presented in Table 1 reveals that the inhibition efficiency of clarithromycin increases with increasing concentration, irrespectively of the concentration of the acid. This also indicates that clarithromycin is an adsorption inhibitor for the corrosion of zinc in H_2SO_4 [40]. We also observed that increasing concentration of H_2SO_4 reduces the inhibition potential of clarithromycin. However, the reduction was not significant ($P > 0.05$).

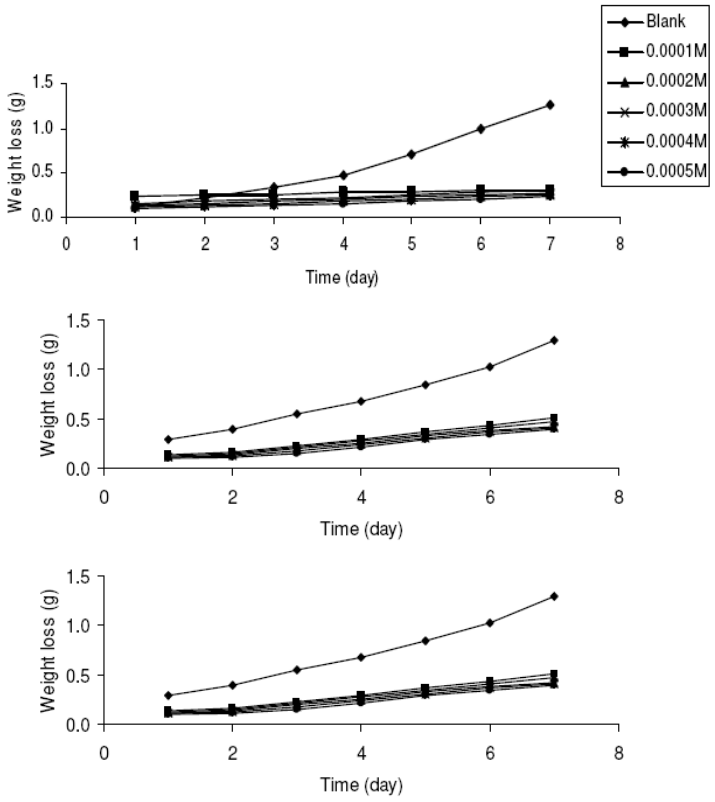

Figure 2. Variation of weight loss with time for the corrosion of Zn in 0.01 M H_2SO_4 containing various concentrations of clarithromycin at (a) 303 K, (b) 313 K, and (c) 323 K.

Effect of temperature

We used the Arrhenius equation to study the effect of temperature on the corrosion of zinc in H_2SO_4. The statement of the Arrhenius theory of reaction can be expressed as equation 5 and upon simplification, we obtained equation 6 [41],

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

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

where CR is the corrosion rate of zinc (calculated from equation 3), A is the pre-exponential factor or the Arrhenius constant, E_a is the activation energy, R is the

gas constant and T is the temperature. Using equation 6, the plots of logCR versus 1/T (Fig. 3a to 3d) were linear, indicating that the slope and intercept are equal to $-E_a/2.303RT$ and logA. Calculated values of E_a are recorded in Table 2.

Table 2. Some thermodynamic parameters for the inhibition of the corrosion of zinc by various concentrations of clarithromycin.

C (M)	0.01 M H_2SO_4				
	E_a (J/mol)	R^2	ΔH_{ads} (J/mol)	ΔS_{ads} (J/mol)	R^{2*}
Blank	3.15	0.9532	-0.87	307.95	0.9943
0.0001	25.74	0.9268	23.08	-257.491	0.8615
0.0002	25.86	0.9406	23.20	-257.248	0.9111
0.0003	26.91	0.9326	24.25	-256.577	0.9278
0.0004	26.41	0.8844	23.75	-252.185	0.9188
0.0005	31.45	0.9654	28.79	-237.005	0.9594
C (M)	0.02 M H_2SO_4				
	E_a (J/mol)	R^2	ΔH_{ads} (J/mol)	ΔS_{ads} (J/mol)	R^{2*}
Blank	4.23	0.9835	-1.57	304.77	0.9005
0.0001	8.63	0.8915	5.98	-309.14	0.7949
0.0002	12.78	0.9775	10.13	-296.50	0.9637
0.0003	14.80	0.8675	12.15	-288.43	0.8138
0.0004	20.15	0.9783	17.50	-273.66	0.9719
0.0005	27.45	0.932	24.79	-251.60	0.9184
C (M)	0.03 M H_2SO_4				
	E_a (J/mol)	R^2	ΔH_{ads} (J/mol)	ΔS_{ads} (J/mol)	R^{2*}
Blank	2.94	0.9271	-1.44	90.31	0.6203
0.0001	18.47	0.9447	15.82	-275.87	0.9268
0.0002	21.03	0.8864	18.37	-266.80	0.8570
0.0003	22.24	0.8567	19.58	-262.39	0.8233
0.0004	23.01	0.8717	20.36	-258.72	0.8424
0.0005	24.98	0.8485	22.32	-252.98	0.818
Con. (M)	0.04 M H_2SO_4				
	E_a (J/mol)	R^2	ΔH_{ads} (J/mol)	ΔS_{ads} (J/mol)	R^{2*}
Blank	9.99	0.9950	-7.34	284.56	0.9913
0.0001	21.18	0.8626	18.52	-267.07	0.8285
0.0002	24.67	0.8580	22.01	-254.626	0.8286
0.0003	24.93	0.9050	22.27	-252.093	0.8844
0.0004	28.62	0.8773	25.67	-241.924	0.8551
0.0005	28.69	0.8692	26.03	-240.986	0.8460

C = concentration of clarithromycin; R^2 = degree of linearity for the Arrhenius plot;
R^{2*} = degree of linearity for the transition state plot.

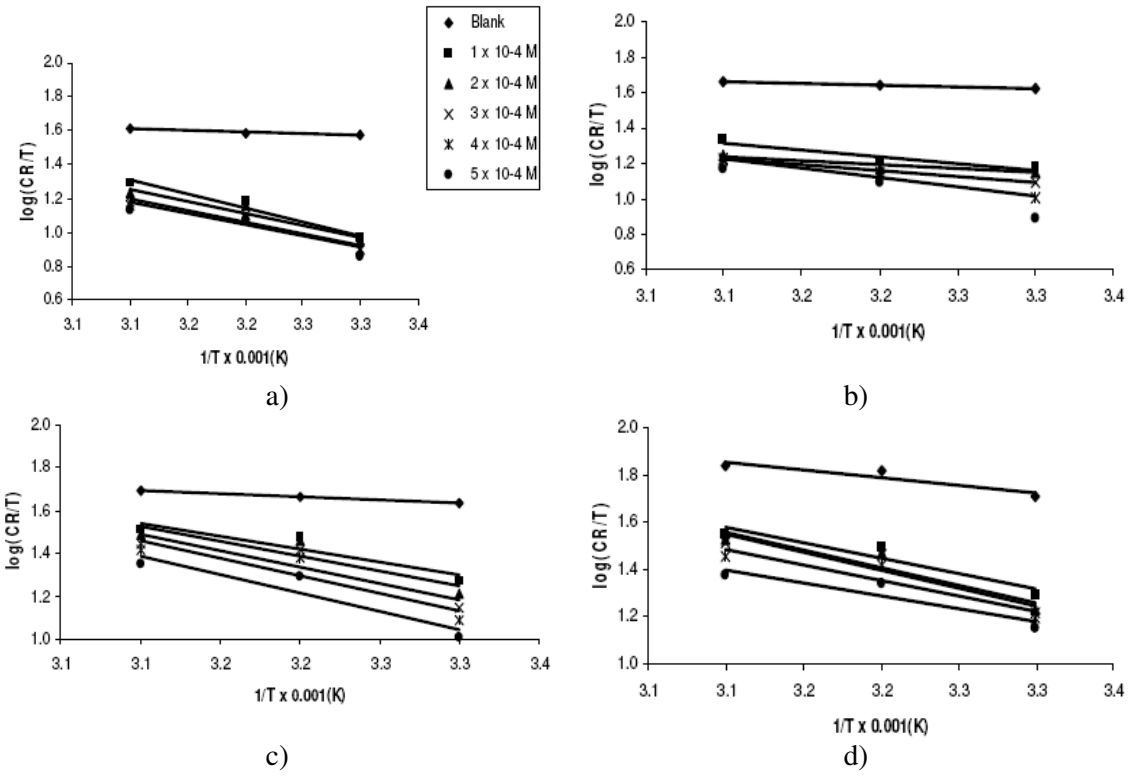

Figure 3. Variation of logCR with 1/T for the inhibition of zinc corrosion [in (a) 0.01 M, (b) 0.02 M, (c) 0.03 M and (d) 0.04 M H_2SO_4] by clarithromycin.

From the results obtained, the activation energies for the blank solutions were lower than those obtained for solutions containing various concentrations of clarithromycin. We also observed that the activation energy tends to increase with increasing concentration of the inhibitor, indicating that there is an increasing of adsorption of the inhibitor as the concentration of the inhibitor is increased. This fact also agrees with the results presented in Table 1, which reveals that the inhibition efficiency of clarithromycin increases with increase in concentration. Within the context of the present findings, we can also state that the mechanism of adsorption of the inhibitor on zinc surface is physical adsorption because the activation energies are less than 80 KJ/mol. E_a values greater than 80 KJ/mol are usually accepted as an evidence for the mechanism of chemical adsorption, whereas E_a values less than 80 KJ/mol support the mechanism of physical adsorption.

Thermodynamic/adsorption considerations

The transition state equation was used to calculate thermodynamic parameters for the adsorption of clarithromycin on zinc surface. According to the transition state equation (given below), the enthalpy and entropy of adsorption of the inhibitor can be related to the corrosion rate of zinc as follows [42],

$$CR = R/Nh\exp(\Delta S_{ads}/R)\exp(-\Delta H_{ads}/RT) \quad (7)$$

where CR is the corrosion rate of zinc, R is the gas constant, N is the Avogadro's number, h is the Planck constant, T is the temperature, ΔS_{ads} and ΔH_{ads} are the

entropy and enthalpy of adsorption of the inhibitor on zinc surface, respectively. Transforming equation 7 into a linear form by taking logarithm of both sides of the equation, equation 8 is obtained,

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

From equation 8, a plot of log(CR/T) versus 1/T is expected to yield a straight line with slope and intercept equal to $\Delta H_{ads}/2.303R$ and ($\log(R/Nh) + \Delta S_{ads}/2.303R$), respectively. Figs. 4a to 4d present the transition state plots for the corrosion of zinc in 0.01, 0.02, 0.03 and 0.04 M H_2SO_4 (in the absence and presence of various concentrations of clarithromycin (as additives) respectively.

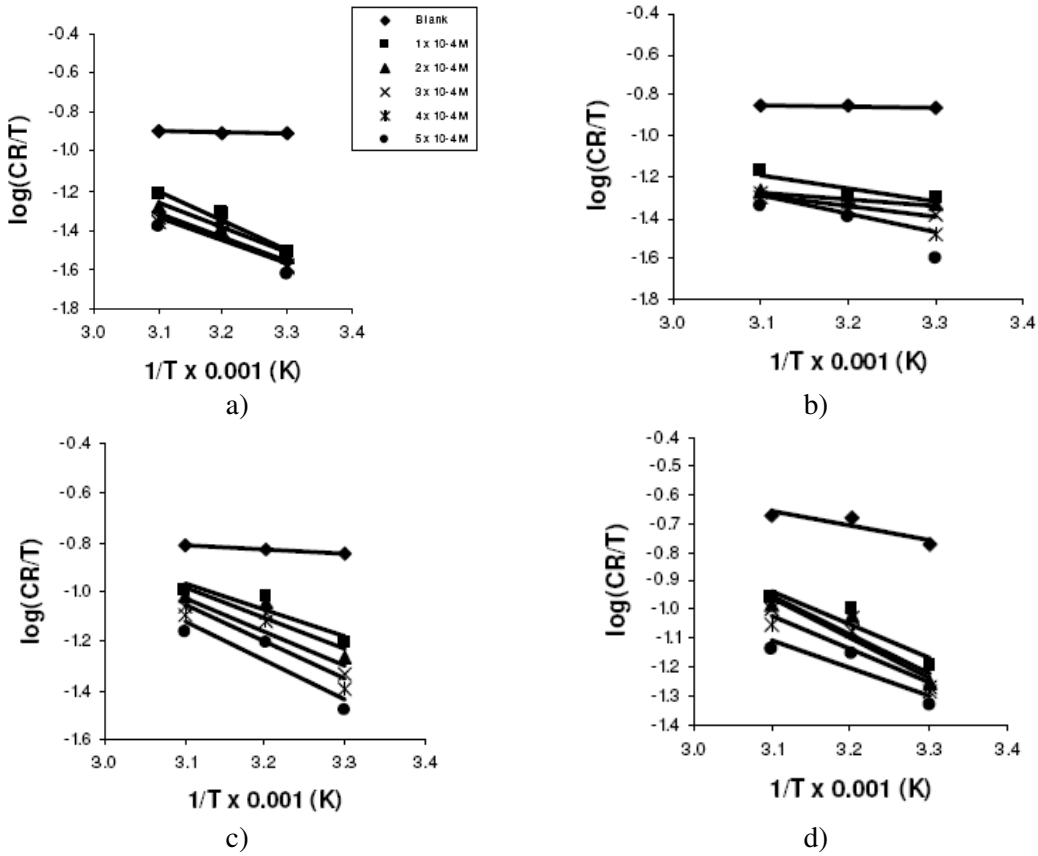

Figure 4. Variation of log(CR/T) with 1/T for the inhibition of zinc corrosion [in (a) 0.01 M, (b) 0.02 M, (c) 0.03 M and (d) 0.04 M H_2SO_4] by clarithromycin.

Values of ΔH_{ads} calculated from slopes of lines on the transition state plots are presented in Table 2. Calculated values of ΔH_{ads} are positive, indicating that the adsorption of the inhibitor on zinc surface is endothermic. The results obtained also reveal an increase in ΔH_{ads} values as the concentration of the inhibitor increases, suggesting a corresponding increase in the heat of adsorption, hence better adsorption, with increasing concentration of the inhibitor. Interestingly, we also noted that there was no significant difference between ΔH_{ads} values and the values of E_a, and the two sets of data correlated strongly ($P>0.05$). This observation can be explained as follows: the Arrhenius equation can be equated with the transition state equation thus,

$$A\exp(-E_a/RT) = RT/Nh \exp(-\Delta H_{ads}/RT)\exp(\Delta S_{ads}/R) \quad (9)$$

From equation 9, we can see that the activation energy is related to the enthalpy of adsorption, while the Arrhenius constant (A) is related to the entropy of adsorption, thus $A = (RT/Nh)\exp(\Delta S_{ads}/R)$, while $\exp(-E_a/RT)=\exp(-\Delta H_{ads}/RT)$. Therefore, we can state that for reactions involving liquids (such as corrosion), $\Delta(PV)$ is negligibly small and since $\Delta H_{ad} = E_a + \Delta(PV)$, values of E_a should approximate ΔH_{ad} values as found in the presence study. On the other hand, values of ΔS_{ads} calculated from the intercepts of lines on the transition state plots (Table 2) were negative and tend to increase with increase in the concentration of the inhibitor. This implies that there is an increase in the degree of orderliness of the inhibitor's molecules with increasing concentration.

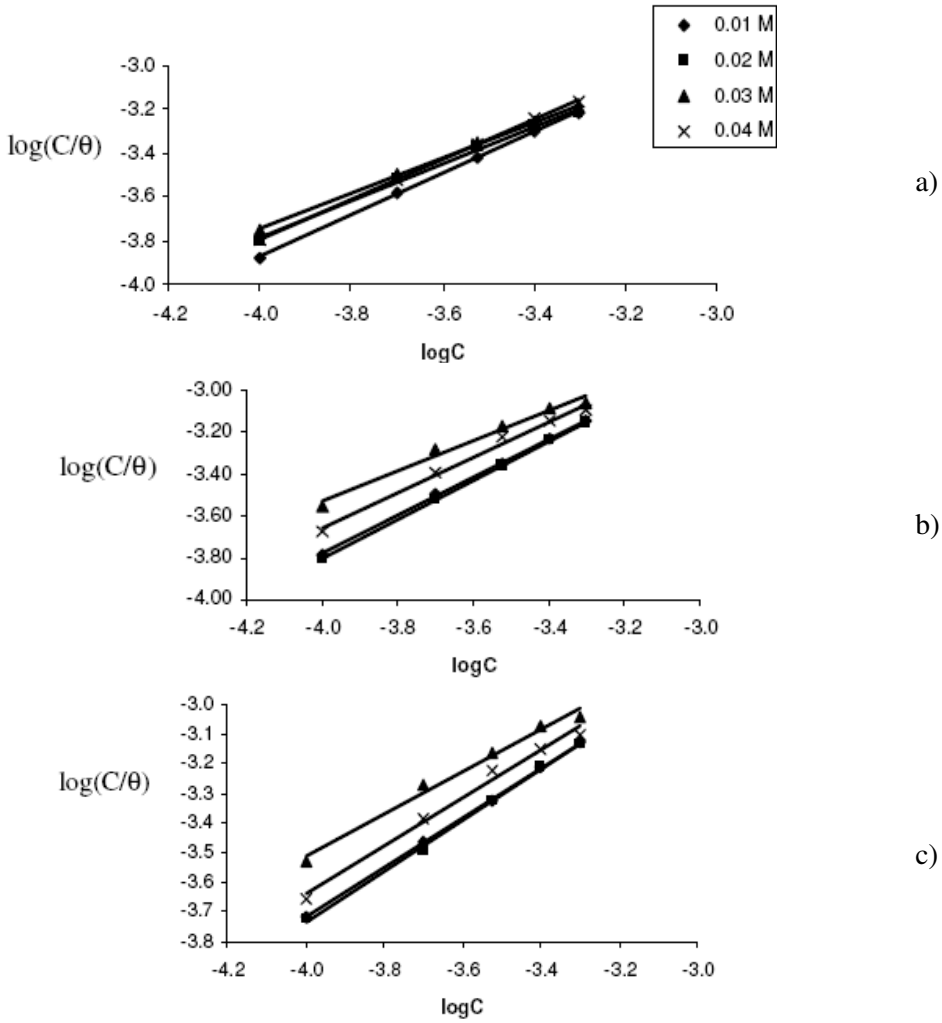

Figure 5. Langmuir isotherm for the adsorption of clarithromycin on zinc surface in various concentrations of H_2SO_4 at (a) 303 K, (b) 313 K and (c) 323 K.

The adsorption characteristics of clarithromycin on zinc surface were studied using adsorption isotherm. Data obtained for degree of surface coverage of the inhibitor (equation 2) were used to fit curves for different adsorption isotherms. The test reveals that the adsorption of clarithromycin on zinc surface can best be

described using Langmuir adsorption isotherm. The assumptions establishing Langmuir adsorption isotherm can be expressed as follows [43]:

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

where C is the concentration (in moles/dm^3) of the inhibitor in the bulk electrolyte, θ is the degree of surface coverage of the inhibitor and K is the adsorption equilibrium constant. Langmuir isotherms for the adsorption of clarithromycin on zinc surface are shown in Fig. 5a to 5c. Values of Langmuir adsorption parameters obtained from the plots are presented in Table 3. The results obtained indicate that the slopes and R^2 values for the plots are very close to unity, which indicates a strong adherence of the assumptions of Langmuir to experimental data.

Table 3. Langmuir adsorption parameters and free energies of adsorption of clarithromycin on the surface of zinc.

	Concentration of H_2SO_4 = 0.01 M			
Temperature (K)	**slope**	**logK**	**ΔG_{ads} (KJ/mol)**	**R^2**
303	0.9563	0.0502	-10.39	0.9998
313	0.9125	0.1317	-11.22	0.9995
323	0.8372	0.3681	-13.04	0.9996
	Concentration of H_2SO_4 = 0.02 M			
Temperature (K)	**slope**	**logK**	**ΔG_{ads} (KJ/mol)**	**R^2**
303	0.8507	0.3863	-12.34	0.9955
313	0.9311	0.0787	-10.90	0.9998
323	0.8577	0.3013	-12.62	0.9981
	Concentration of H_2SO_4 = 0.03 M			
Temperature (K)	**slope**	**logK**	**ΔG_{ads} (KJ/mol)**	**R^2**
303	0.8144	0.4882	-12.93	0.9889
313	0.7206	0.6484	-14.31	0.9803
323	0.7107	0.6665	-14.88	0.9877
	Concentration of H_2SO_4 = 0.04 M			
Temperature (K)	**slope**	**logK**	**ΔG_{ads} (KJ/mol)**	**R^2**
303	0.9115	0.1474	-10.95	0.9996
313	0.8415	0.2903	-12.17	0.9905
323	0.8098	0.4013	-13.24	0.9882

The equilibrium constant of adsorption (K) obtained from the intercepts of Langmuir adsorption isotherm is related to the free energy of adsorption (ΔG_{ads}) as follows [44],

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

where 55.5 is the molar concentration of the acid in the solution. Values of ΔG_{ads} calculated from equation 11 are also presented in Table 3. The negative values obtained for ΔG_{ads} suggest that the inhibitor's molecules are strongly adsorbed on zinc surface. The values also indicate a spontaneous adsorption of the inhibitor molecules and usually characterize their strong interaction with the metal surface. The value of ΔG_{ads} of -40 KJ/mol is usually accepted as a threshold value between chemisorption and physiosorption [45]. The values of ΔG_{ads} obtained in our study are below -40 KJ/mol (ΔG_{ads} values ranged from -10.39 to -13.04

KJ/mol, -10.90 to -12.62 KJ/mol, -12.93 to -14.88 KJ/mol and from -10.95 to -13.54 KJ/mol at H_2SO_4 concentrations of 0.01, 0.02, 0.03 and 0.04 M, respectively). This is consistent with electrostatic interaction between the charged molecules and the charged metal which are indicative of physical adsorption mechanism.

Conclusion

Clarithromycin is a good inhibitor for the corrosion of zinc in H_2SO_4. The inhibitor best functions at room temperature and its behaviour can be adequately modelled using thermodynamic and adsorption principles. The use of clarithromycin as an inhibitor for zinc corrosion is therefore advocated in this work.

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