

Inhibition of the Corrosion of Zinc in H₂SO₄ by 9-deoxy-9a-aza-9a-methyl-9a-homoerythromycin A (Azithromycin)

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Abstract

Inhibition of the corrosion of zinc in various concentrations (0.01 to 0.05 M) of H₂SO₄ was studied using weight loss and hydrogen evolution methods of monitoring corrosion. The results revealed that various concentrations of azithromycin (0.0001 to 0.0005 M) inhibited the corrosion of zinc in H₂SO₄ at different temperatures (303 to 333 K). The concentration of H₂SO₄ did not exert significant impact on the inhibition efficiency of azithromycin, but inhibition efficiencies were found to decrease with increase in the concentration of the inhibitor. Values of inhibition efficiency obtained from the weight loss measurements correlated strongly with those obtained from the hydrogen evolution measurements. The activation energies for the corrosion of zinc inhibited by azithromycin were higher than the values obtained for the blank. Thermodynamic data revealed that the adsorption of azithromycin on the surface of zinc was endothermic (values of enthalpies of adsorption were positive), spontaneous (values of free energies of adsorption were negative) and was consistent with the adsorption model of Langmuir.

Keywords: Corrosion inhibition, zinc, azithromycin.

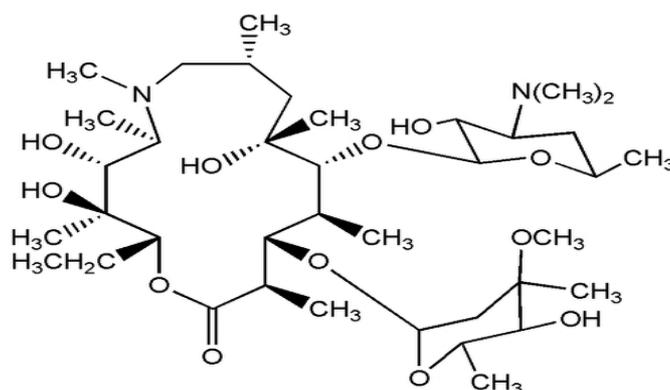
Introduction

Zinc is one of the most widely used metal and is often attacked by aggressive media such as acids, bases and salt solutions [1-4]. For scale removal and cleaning of zinc surfaces with acids solution, the use of an inhibitor is necessary.

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A survey of literature reveals that there are very few inhibitors for the corrosion of zinc in H_2SO_4 .

Most effective inhibitors are organic compounds containing electronegative functional groups and π -electrons in triple or conjugated double bonds [5-10]. Recently, some drugs have been found to be good corrosion inhibitors [11-13]. However, the use of azithromycin as a corrosion inhibitor has not been reported elsewhere. Azithromycin is the first member of a class of macrolides antibiotics called azide. The drug is a very efficient therapeutic agent for the oral treatment of sexually transmitted diseases, typical and atypical pneumonia, infection of the inferior and superior breathing tract and structural infection of the skin [14]. The chemical formula of the compound is $C_{38}H_{72}N_2O_{12}$ and its molar mass is equal to 748.88 g/mol. The chemical structure of azithromycin is shown below. From the structure, it is indicative that the azithromycin molecule contains hetero atoms and may be a good inhibitor for the corrosion of zinc in H_2SO_4 . The present study is aimed at investigating the inhibitive and adsorption properties of azithromycin for the corrosion of zinc in H_2SO_4 .



Chemical structure of azithromycin

Experimental details

Gravimetric method

In the weight loss experiment, the pre-cleaned zinc coupon was dipped in 20 mL of the test solution maintained at 303 and 333 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. From the weight loss, 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.

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

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

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

where %I is the inhibition efficiency of azithromycin, CR is the corrosion rate of zinc in $\text{gh}^{-1}\text{cm}^{-3}$, W_1 and W_2 are the weight loss of zinc in the absence and presence of the inhibitor, respectively, W is the difference in weight (in g) before and after immersion (i.e, $W = W_2 - W_1$), t is the period of immersion in hours and A is the area of the zinc coupon in square meter.

Gasometric method

Gasometric measurements were carried out at 303 and 333K as described previously [10]. From the volume of hydrogen evolved per minute, inhibition efficiency (%I), and degree of surface coverage (θ) were calculated using Equations 4 and 5, respectively.

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

$$\theta = \left(1 - \frac{V_{Ht}^I}{V_{Ht}^o} \right) \quad (5)$$

where V_{Ht}^I and V_{Ht}^o are the volume of H_2 gas evolved at time 't' for inhibited and uninhibited solution, respectively.

Results and discussion

Figure 1 shows the variation of weight loss with time for the corrosion of zinc in 0.05 M H_2SO_4 at 303, 313 and 323 K, respectively. The plots revealed that weight loss of zinc increased with increase in temperature and with the period of contact, indicating that the rate of corrosion of zinc in H_2SO_4 increased with increase in temperature and with the period of contact. However, in the presence of various concentrations of azithromycin, weight loss of zinc was found to decrease with increase in the concentration of azithromycin, indicating that azithromycin retarded the corrosion of zinc in H_2SO_4 and that the rate of corrosion of zinc in the presence of azithromycin decreased as the concentration of azithromycin increases. At other concentrations of H_2SO_4 (0.01 to 0.04), similar trend was followed (plots of weight loss versus time not shown).

Table 1 shows the corrosion rate of zinc in H_2SO_4 and the inhibition efficiencies of azithromycin for the corrosion of zinc in H_2SO_4 . The results revealed that the corrosion rates of zinc decreased with increase in the concentration of azithromycin, while the inhibition efficiency increased with increase in the concentration of azithromycin, indicating that azithromycin inhibited the corrosion of zinc in H_2SO_4 . It was also found that there was no significant difference between values of inhibition efficiencies obtained at difference concentrations of H_2SO_4 . Values of inhibition efficiency obtained from hydrogen evolution measurements were 59.9, 62.5, 65.8, 72.3 and 79.3 at azithromycin concentrations of 0.0001, 0.0002, 0.0003, 0.0004 and 0.0005 M, respectively.

These values were comparable to average values obtained from weight loss measurements.

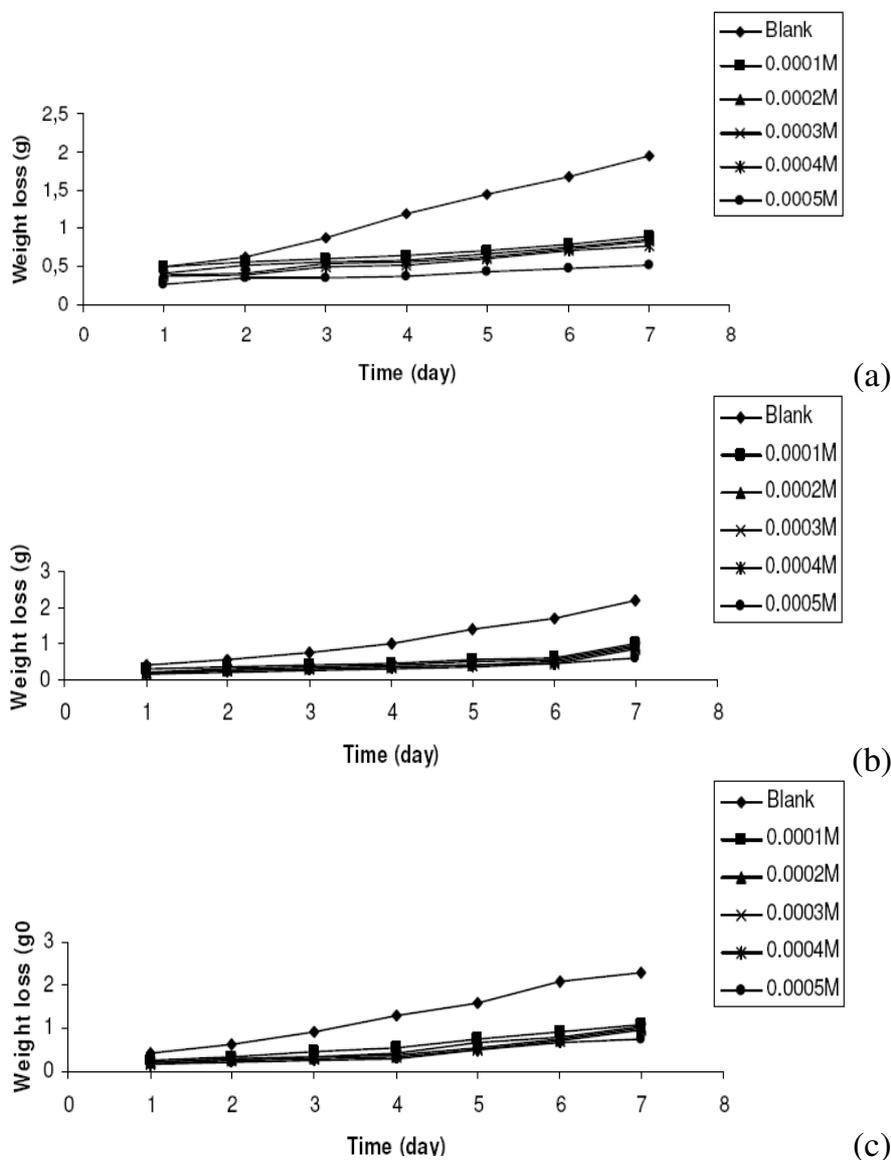


Figure 1. Variation of weight loss with time for the the corrosion of Zn in 0.05 M tetraoxosulphate (VI) acid containing various concentrations of azithromycin at (a) 303, (b) 313 and (c) 323 K.

Kinetic treatment of data obtained from weight loss measurements revealed that the plots of $-\log(\text{weight loss})$ versus time (Fig. 2a to 2c) were linear for all concentrations of the acid and the inhibitor, indicating that the corrosion of zinc in H_2SO_4 (in the presence and absence of azithromycin) is of the first order [11].

Table 1. Corrosion rates ($\text{gcm}^{-2}\text{h}^{-1}$) of zinc and inhibition efficiencies of azithromycin for the corrosion of zinc in various concentrations of H_2SO_4 .

303 K		0.01 M H_2SO_4		0.02 M H_2SO_4		0.03 M H_2SO_4		0.04 M H_2SO_4		0.05 M H_2SO_4	
$C \times 10^{-4}$ (M)	%I	$CR \times 10^{-4}$									
1	68.50	11.9	65.00	1.46	55.00	2.02	48.55	2.65	53.57	2.71	
2	75.54	9.23	69.29	1.28	59.31	1.76	56.07	2.26	56.12	2.56	
3	81.89	6.85	72.14	1.16	61.38	1.67	60.69	2.02	57.14	2.50	
4	83.46	6.25	79.29	0.86	62.07	1.64	64.16	1.85	60.71	2.29	
5	90.55	3.57	82.14	0.74	66.21	1.46	65.90	1.70	73.47	1.55	
313 K		0.01 M H_2SO_4		0.02 M H_2SO_4		0.03 M H_2SO_4		0.04 M H_2SO_4		0.05 M H_2SO_4	
$C \times 10^{-4}$ (M)	%I	$CR \times 10^{-4}$									
1	60.00	1.55	57.72	1.88	48.72	2.38	52.02	2.83	54.55	2.98	
2	66.15	1.31	62.42	1.67	56.41	2.02	57.07	2.53	56.82	2.83	
3	68.46	1.22	65.10	1.55	61.54	1.79	62.12	2.23	59.09	2.68	
4	69.23	1.19	66.44	1.49	64.74	1.64	65.66	2.02	61.36	2.53	
5	78.46	0.83	67.11	1.40	66.67	1.55	69.70	1.79	72.73	1.79	
323 K		0.01 M H_2SO_4		0.02 M H_2SO_4		0.03 M H_2SO_4		0.04 M H_2SO_4		0.05 M H_2SO_4	
$C \times 10^{-4}$ (M)	%I	$CR \times 10^{-4}$									
1	57.66	1.73	54.84	2.08	46.99	2.62	52.27	3.13	52.38	3.27	
2	62.04	1.55	58.06	1.93	53.01	2.32	54.55	2.98	54.55	3.13	
3	64.90	1.43	61.29	1.79	57.83	2.08	56.82	2.83	56.71	2.98	
4	67.15	1.34	64.52	1.64	60.84	1.93	61.36	2.33	58.87	2.83	
5	70.07	1.22	66.45	1.55	63.86	1.79	68.18	2.08	67.53	2.23	

This also implies that the relationship expressed by Equations 6 and 7 is applicable to the inhibited and uninhibited corrosion reactions of zinc [12-14]

$$-\log(\text{weight loss})=k_1t/2.303 \quad (6)$$

$$t_{1/2} = 0.693/k_1 \quad (7)$$

where k_1 is the first order rate constant for the corrosion of zinc, t is the time (in days) and $t_{1/2}$ is the half life of the reaction. Values of k_1 and $t_{1/2}$ calculated from Equations 5 and 7 were found to vary with temperature but were constant at a given concentration of azithromycin, indicating that the assumptions of the rate model are applicable to the corrosion of zinc. The results also indicated that azithromycin increased the half life of zinc in H_2SO_4 hence it is a good inhibitor for the corrosion of zinc [15-16].

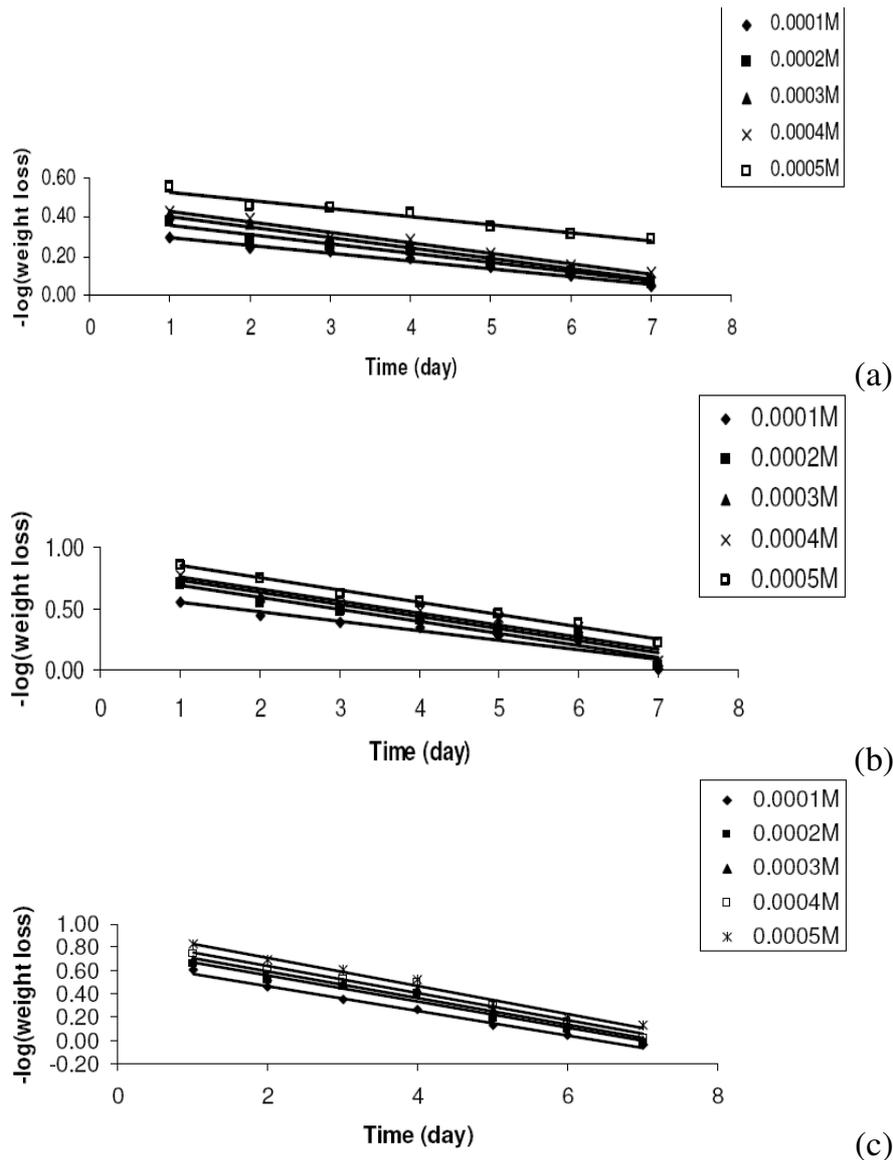


Figure 2. Kinetic plots for the corrosion of Zn in 0.05 M of tetraoxosulphate (VI) acid containing various concentrations of azithromycin at (a) 303, (b) 313 and (c) 323 K.

The effect of temperature on the corrosion of zinc in H_2SO_4 (in the absence and presence of azithromycin) was studied using the Arrhenius Equation (Equation 8) [17-20],

$$\text{CR} = A \exp(-E_a/RT) \quad (8)$$

where A is Arrhenius or pre-exponential constant, E_a is the activation energy, R is the gas constant and T is the temperature. Taking the logarithm of both sides of Equation 8, Equation 9 was obtained.

$$\log k = \log A - E_a/2.303RT \quad (9)$$

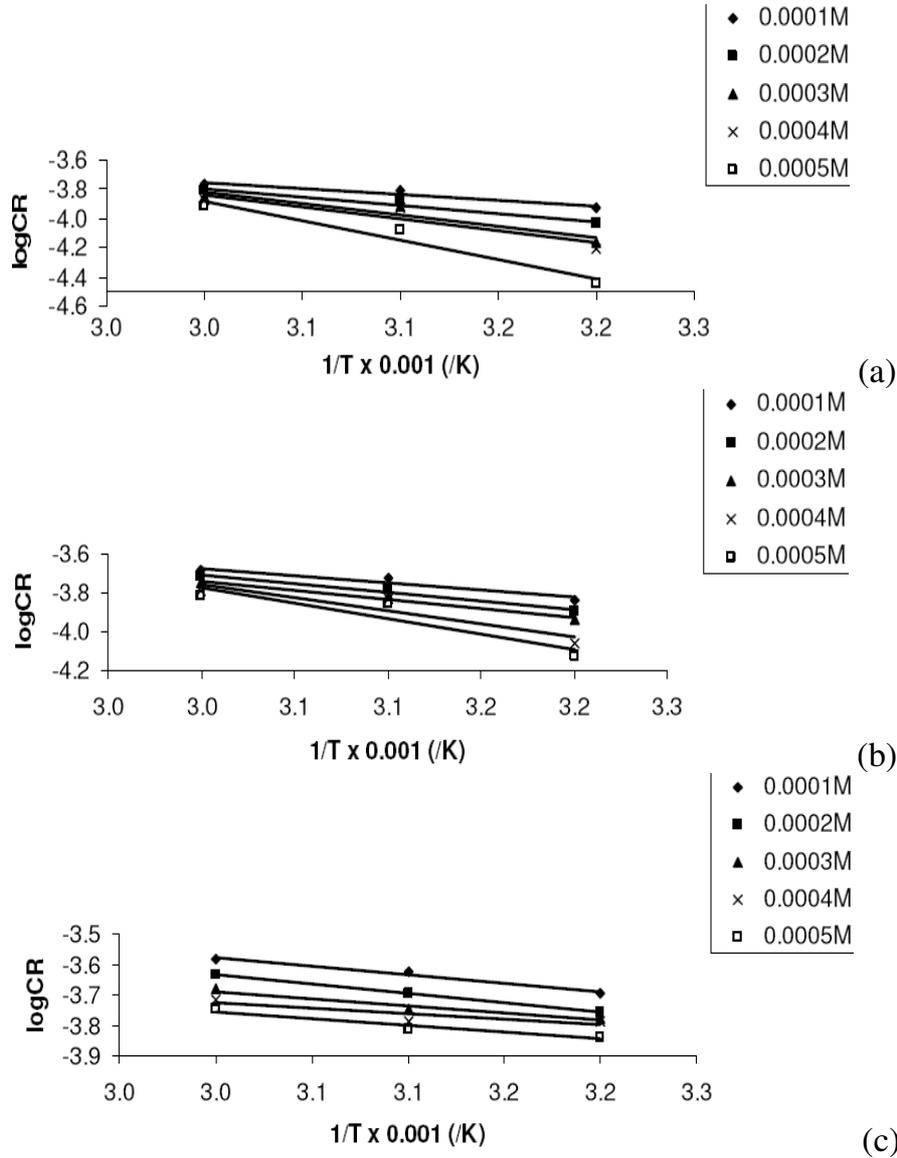


Figure 3. Arrhenius plot for the corrosion of Zn in (a) 0.01 M, (b) 0.02 M and (c) 0.03 M tetraoxosulphate (VI) containing various concentrations of azithromycin.

The plots of $\log k$ versus $1/T$ were linear and from the slopes, values of E_a were calculated (Table 2). Figs. 3a to 3c show Arrhenius plots for the corrosion of zinc in 0.03 M H_2SO_4 inhibited by azithromycin (plots for other concentrations of acid are not shown). Values of the activation energies calculated from the slopes of the Arrhenius plots ranged from 3.15 to 9.99 J/mol and from 6.87 to 51.08 J/mol for the blank and inhibited systems, respectively. These values are less than the threshold value of 80 KJ/mol required for a chemical adsorption mechanism hence the mechanism of adsorption of azithromycin on the surface of zinc is physical adsorption [2]. The activation energies were also found to

increase as the concentration of azithromycin increases, indicating that the ease of adsorption also increased with increase in the concentration of the inhibitor. The thermodynamic parameters (enthalpy and entropy of adsorption) for the adsorption of azithromycin on the surface of zinc were calculated using the transition state equation (Equation 10) [17]

$$CR = RT(\exp(\Delta S_{\text{ads}}/R)\exp(-\Delta H_{\text{ads}}/RT)/Nh) \quad (10)$$

Table 2. Activation energy and thermodynamic parameters for the adsorption of azithromycin on the surface of zinc.

Con. (M)	0.01 M H ₂ SO ₄				
	E _a (J/mol)	R ²	ΔH _{ads}	ΔS _{ads}	R ^{2*}
0.0001	15.45	0.9464	12.79	-279.11	0.9246
0.0002	21.51	0.9599	18.84	-261.80	0.9489
0.0003	30.59	0.9018	27.93	-234.89	0.885
0.0004	31.69	0.8627	29.03	-231.98	0.8411
0.0005	51.08	0.9543	48.43	-174.65	0.9496
Con. (M)	0.02 M H ₂ SO ₄				
	E _a (J/mol)	R ²	ΔH _{ads}	ΔS _{ads}	R ^{2*}
0.0001	14.83	0.9471	12.17	-279.41	0.9245
0.0002	17.18	0.9748	14.52	-273.02	0.9657
0.0003	17.91	0.9638	15.25	-271.45	0.9514
0.0004	26.61	0.8588	23.95	-245.65	0.8320
0.0005	30.45	0.8513	27.79	-234.49	0.8272
Con. (M)	0.03 M H ₂ SO ₄				
	E _a (J/mol)	R ²	ΔH _{ads}	ΔS _{ads}	R ^{2*}
0.0001	6.95	0.9779	8.06	-289.95	0.9626
0.0002	8.42	0.9999	8.94	-288.37	0.9999
0.0003	9.28	0.9537	6.62	-296.39	0.9110
0.0004	10.72	0.7500	4.29	-304.11	0.5304
0.0005	11.61	0.9462	5.76	-299.09	0.8893
Con. (M)	0.04 M H ₂ SO ₄				
	E _a (J/mol)	R ²	ΔH _{ads}	ΔS _{ads}	R ^{2*}
0.0001	6.87	0.9854	4.22	-300.16	0.9600
0.0002	8.54	0.9888	8.75	-286.98	0.9804
0.0003	11.41	0.9460	11.25	-280.05	0.9186
0.0004	13.11	0.9458	10.46	-283.32	0.9162
0.0005	13.90	0.9229	5.88	-298.62	0.8478
Con. (M)	0.05 M H ₂ SO ₄				
	E _a (J/mol)	R ²	ΔH _{ads}	ΔS _{ads}	R ^{2*}
0.0001	7.25	1.0000	5.23	-296.69	0.9999
0.0002	7.88	1.0000	5.64	-295.83	1.0000
0.0003	8.30	0.9857	4.59	-299.44	0.9632
0.0004	8.73	0.9988	6.07	-295.38	0.9972
0.0005	15.23	0.9843	12.57	-277.96	0.9766

R² = degree of linearity for the Arrhenius plot. R^{2*} = degree of linearity for the transition state plot.

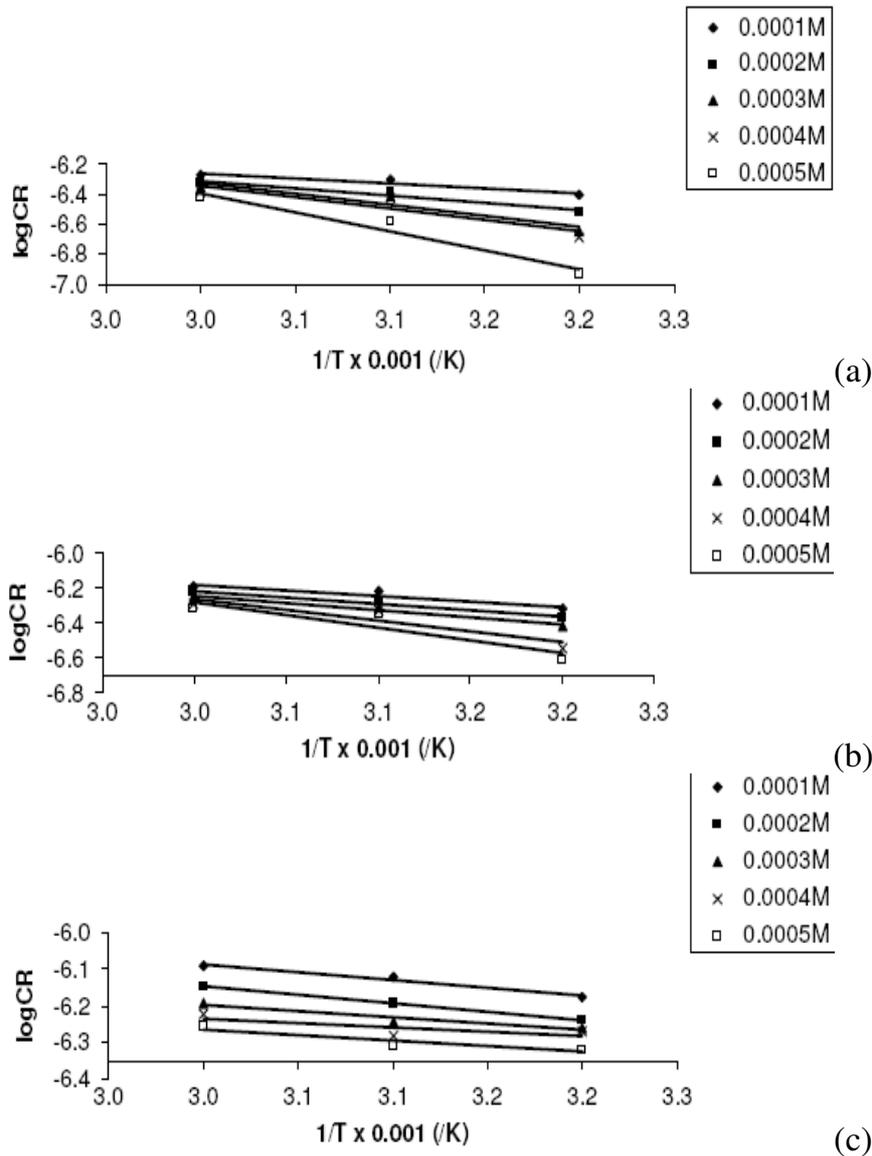


Figure 4. Transition state plot for the corrosion of Zn in 0.01 M (a), 0.02 M (b) and 0.03 M (c) tetraoxosulphate (VI) containing various concentrations of azithromycin.

where ΔH_{ads} is the enthalpy of adsorption, ΔS_{ads} is the entropy of adsorption, R is the gas constant, T is the temperature, N is the Avogadro's number and h is the Planck constant. Rearranging and taking the logarithm of both sides of Equation 10 yields Equation 11:

$$\log(CR/T) = \log(R/Nh) + \Delta S_{\text{ads}}/2.303R - \Delta H_{\text{ads}}/2.303RT \quad (11)$$

The plots of $\log(CR/T)$ versus $1/T$ were linear indicating that the slope and intercept are equal to $\Delta H_{\text{ads}}/2.303R$ and $(\log(R/Nh) + \Delta S_{\text{ads}}/2.303R)$, respectively. Figs. 4a to 4c show the transition state plots for the corrosion of zinc in 0.03 M H_2SO_4 as a representative plot. Values of ΔH_{ads} and ΔS_{ads} deduced from the slopes and intercepts of the plots are recorded in Table 2. From the results, it was found that the adsorption of azithromycin on the surface of zinc is endothermic

(ΔH_{ads}) and there was an association of the inhibitor's molecules instead of dissociation (ΔS_{ads}).

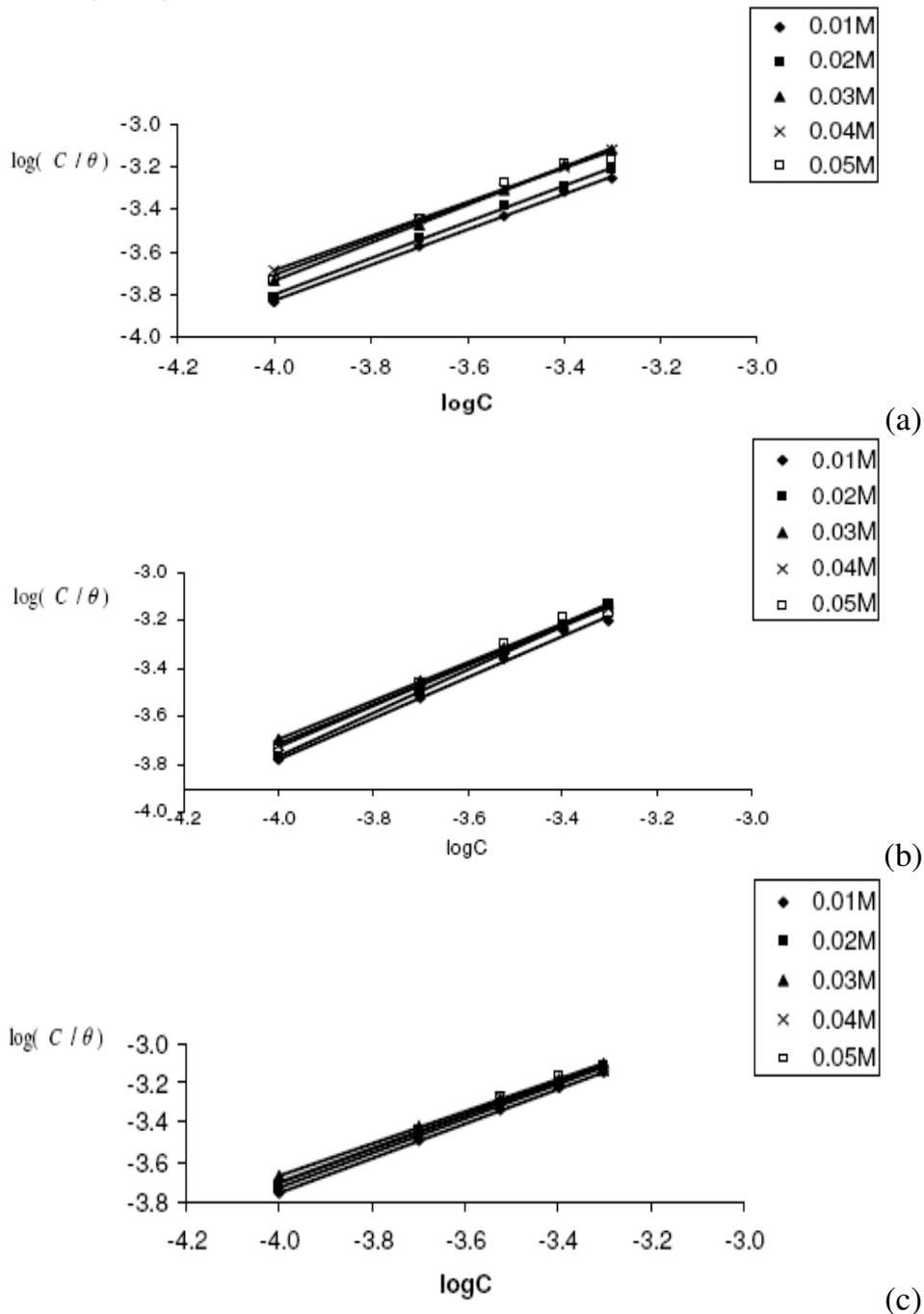


Figure 5. Langmuir isotherm for the adsorption of azithromycin on the surface of Zn immersed in various concentrations of tetraoxosulphate (VI) at (a) 303, (b) 313 and (c) 323 K.

Adsorption isotherm is very important in studying the adsorption characteristics of an inhibitor. Values of degree of surface coverage calculated from weight loss data were used to fit curves for different adsorption isotherms, including Temkin, Langmuir, Freundlich, Frumkin and Florry-Huggins ones. The test indicated that Langmuir adsorption isotherm best described the adsorption characteristics of azithromycin on the surface of zinc.

The Langmuir adsorption isotherm can be expressed according to Equation 12 [18]

$$C/\theta = 1/K + C \quad (12)$$

where C is the concentration of the inhibitor in the bulk electrolyte, θ is the degree of surface coverage of the inhibitor and K is the equilibrium constant of adsorption. Taking the logarithm of both sides of Equation 12, Equation 13 was obtained

$$\log(C/\theta) = \log C - \log K \quad (13)$$

The plots of $\log(C/\theta)$ versus $\log C$ were linear indicating that the assumptions of Langmuir adsorption isotherm are applicable to the adsorption of azithromycin on the surface of mild steel.

Table 3. Langmuir adsorption parameters and free energy of adsorption of azithromycin on the surface of zinc.

		303 K			
C of H ₂ SO ₄ (M)	slope	logK	ΔG_{ads}	R ²	
0.01	0.8354	0.4912	-11.00	0.9999	
0.02	0.8542	0.3878	-12.10	0.9978	
0.03	0.8958	0.1565	-12.34	0.9993	
0.04	0.8068	0.4614	-12.77	0.9998	
0.05	0.8413	0.3457	-12.94	0.9827	
		313 K			
C of H ₂ SO ₄ (M)	slope	logK	ΔG_{ads}	R ²	
0.01	0.8582	0.3420	-11.31	0.9960	
0.02	0.9041	0.1475	-12.30	0.9998	
0.03	0.8015	0.4840	-12.48	0.9997	
0.04	0.8198	0.4312	-13.01	0.9992	
0.05	0.8524	0.3116	-13.33	0.9881	
		303 K			
C of H ₂ SO ₄ (M)	slope	logK	ΔG_{ads}	R ²	
0.01	0.8825	0.2287	-12.11	0.9998	
0.02	0.8790	0.2183	-12.18	0.9995	
0.03	0.8092	0.4333	-12.25	0.9999	
0.04	0.8499	0.3042	-12.64	0.9934	
0.05	0.8662	0.2414	-13.44	0.9926	

Figs. 5a to 5c show representative plots for Langmuir adsorption isotherms. Values of adsorption parameters deduced from Langmuir plots are recorded in Table 3. The application of Langmuir adsorption isotherm to the adsorption of azithromycin implies that there is no interaction between the adsorbed species.

The equilibrium constant of adsorption is related to the free energy of adsorption (ΔG_{ads}) according to Equation 14 [19]

$$\Delta G_{\text{ads}} = -2.303RT \log(55.5K) \quad (14)$$

Values of K obtained from Langmuir adsorption isotherm were used to calculate the free energy of adsorption of azithromycin on the surface of mild steel. Calculated values of ΔG_{ads} were found to be negative and less than -40 KJ/mol, indicating that the adsorption of azithromycin on the surface of zinc is spontaneous and proceeded via the mechanism of physical adsorption [19-20].

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