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RESEARCH ARTICLE

Inhibitive Effect of Dirithromycin on the Corrosion of Zinc in Tetraoxosulphate(VI) Acid Medium

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Abstract: The inhibitive effect by dirithromycin, an antibacterial drug, on the corrosion of zinc has been investigated using weight loss method. The results obtained indicate that clindamycin inhibits zinc corrosion in tetraoxosulphate(VI) acid (0.01 to 0.04 M) media. The inhibition efficiency increased with increasing inhibitor's concentration. Kinetic, thermodynamic and adsorption parameters were determined and discussed. The uninhibited corrosion of zinc followed first order kinetics; while the presence of dirithromycin increased the enthalpy of activation, $\Delta H^{\ddagger}$ and therefore made corrosion less probable. The calculated $\Delta G^{\ddagger}$ values for the corrosion processes were positive, but increased in the presence of dirithromycin, suggesting that the activated complex was rather unstable. The adsorption of dirithromycin on zinc surface was exothermic, spontaneous and was best described by Langmuir adsorption isotherm. The calculated values of activation energies and free energies of adsorption indicate that the adsorption process supports the mechanism of physical absorption.

Keywords: Adsorption, Corrosion kinetics, Inhibition, Dirithromycin, Inhibition Efficiency, Activation thermodynamics

Introduction

Corrosion is the gradual degradation of materials, especially metals, by chemical reaction with their environment. Degradation implies deterioration of physical properties of the material which can be a weakening of the material due to a loss of cross-sectional area; it can be the shattering of a metal due to hydrogen embrittlement, or it can be the cracking of a polymer due to sunlight exposure. Metallic zinc is a metal with several industrial applications: it is used in the production of alloys and in galvanizing to protect steel structures and it is still present as a chemical additive in rubber and paints. Zinc is often destroyed by contact with aggressive media such as bases, acids and salt solutions. The treatment of zinc with acidic solutions cannot be completely avoided, as this is necessary for scale removal and cleaning of zinc surfaces. Consequently, corrosion prevention of zinc has become a subject of practical, industrial and economic significance[1-3]. Corrosion prevention can take a number of forms depending on the circumstances of the metal being corroded, and the familiar corrosion prevention techniques include: cathodic protection, coating, plating and corrosion inhibition, to mention but a few.

A corrosion inhibitor is a chemical compound that, when added to a liquid or gas, decreases the corrosion rates of a material, typically a metal or an alloy. A common mechanism for inhibiting corrosion involves formation of a coating, often a passivation layer, which prevents access of the corrosive substance to the metal.

The literature is robust on the study of corrosion inhibition of zinc in acidic solutions using organic compounds containing hetero atoms (N, O, S, or P) and centres for π-electrons in their aromatic or long carbon chain system.

The presence of n- and π-electrons provides enhances the adsorption of inhibitors on the metal surfaces. Several eco-friendly inhibitors, which are extracts from naturally occurring plants proved very effective as metal corrosion inhibitors[4-8]. Recently, research on eco-friendly inhibitors has been extended to the use of drugs. However, the use of dirithromycin as corrosion inhibitor for zinc has not been reported in the literature. Dirithromycin (Figure 1) is a macrolide glycopeptide antibiotic; it is a 14-membered lactone ring macrolide and is the C9-oxazine derivative of erithromycylamine. Dirithromycin has been indicated in the treatment of mild-to-moderate infections caused by susceptible strains of microorganisms: acute bacterial exacerbations of chronic bronchitis, secondary bacterial infection of acute bronchitis, community-acquired pneumonia, pharyngitis/tonsillitis, and uncomplicated skin and skin structure infections[9].

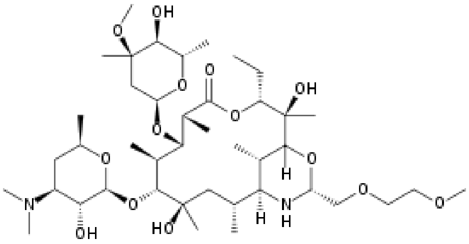

Figure 1. Structure of dirithromycin

The presence of many *n* electron-carrying oxygen atoms in form of hetero atom and hydroxyl groups, as well as amino groups in the structure of should facilitate its adsorption onto zinc surface. In this work, we describe the corrosion inhibition tendencies of dirithromycin, as well as the effects of temperature and acid concentration on the inhibition process.

Experimental

Zinc sheets {(W%): zinc (99.993), lead (0.001), iron (0.002), cadmium (0.001) and copper (0.003)} were purchased from the open market. Dirithromycin was supplied by Rufus Obi Pharmaceutical Company and used without further purification. Tetraoxoxulphate(VI) acid (H_2SO_4) was purchased from SAARCHEM. Water was freshly distilled. Acetone, benzene and ethanol (Aldrich) were A.R. grades.

Preparation of coupons

Zinc specimens were mechanically pressed and cut into coupons of dimensions 5x4 cm^2, with a small hole of about 3 mm diameter just near one end of the specimen. Each coupon was polished by buffing and degreased in benzene and ethanol. They were then dipped in acetone and allowed to dry in air. The weight of each coupon was taken before being preserved in desiccators over silica gel beds.

Weight loss experiments

The zinc coupons were suspended in 200 cm^3 solutions of H_2SO_4 contained in 250 cm^3 beakers using a Pyrex glass hook. The weight loss experiments were carried out in various concentration of H_2SO_4 (0.01, 0.02, 0.03 and 0.04 M) in the absence and presence of dirithromycin (different concentrations: $1x10^{-4}$ to $5x10^{-4}$ M) and at different temperatures (303, 313 and 323 K). The test solutions were maintained in a thermostated bath for 24 h, after which each coupon was washed in 5% chromic acid containing 0.2% $BaCO_3$[10], rinsed with distilled water followed by acetone and then dried in air. The coupons were then weighed again to determine the weight loss due to corrosion. From the weight loss experiment data, the following parameters were evaluated:

- Corrosion rates and order of reaction with respect to H_2SO_4
- Fractional surface coverage of dirithromycin on zinc surface (θ) and subsequently the equilibrium constant (K^o_{ads}), enthalpy (ΔK^o_{ads}), entropy ΔS^o_{ads}) and free energy of adsorption (ΔG^o_{ads}).
- Inhibition efficiency (IE%) of dirithromycin
- Arrhenius parameters - Activation energy and pre-exponential factor (E_a and A respectively)
- Thermodynamic functions (enthalpy, entropy and free energy) of activation ($\Delta H^\ddagger$, $\Delta S^\ddagger$ and $\Delta G^\ddagger$ respectively).

Data Analyses

Corrosion rates (ν_{corr})

Corrosion rates were calculated at (i) different H_2SO_4 concentrations, different dirithromycin concentrations and (iii) different temperatures; according to Equation 1:

$$\nu_{corr} = \frac{w}{A.t} \tag{1}$$

Where *W* is the weight loss of zinc due to corrosion (g), *A*, the cross-section area of the zinc coupon (cm^2) and *t*, the immersion time (h).

Determination of reaction order

The differential method was used in the determination of reaction order. This method involves measuring the initial corrosion rates at different H_2SO_4 concentrations.
The corrosion rate is represented as:

$$\nu_{corr} = k\,[Zn]^x[H_2SO_4]^y \tag{2}$$

Where k is the corrosion rate constant. x and y are the orders of the reaction with respect to zinc and H_2SO_4, respectively.

log ν_{corr} values were then plotted against log [H_2SO_4] in accordance with Equation (3)

$$\text{Log}\ \nu_{corr} = \text{Log}\ k + x\ \text{Log}\ [Zn] + y\ \text{Log}\ [H_2SO_4] \tag{3}$$

Equation (3) can be rewritten as:

$$\text{Log}\ \nu_{corr} = C + y\ \text{Log}\ [H_2SO_4] \tag{4}$$

$$\text{Where } C = \log k + x \log [Zn] \text{ (or } C = \log k[Zn]^x) \tag{5}$$

The slope of the plot is the order of reaction with respect to H_2SO_4.

Adsorption parameters

θ, the fractional surface coverage was determined at different temperatures and dirithromycin concentrations according to Equation 6:

$$\theta = 1 - \frac{w_t}{w_U} \tag{6}$$

Where W_i and W_u are the inhibited and uninhibited weight losses due to corrosion. The Langmuir adsorption isotherm is described by the equation:

$$\log\left(\frac{C}{\theta}\right) = \log C - \log K_{ads}^{o} \tag{7}$$

Where C is the concentration of the inhibitor, clindamycin, *i.e.* [Clin], and K_{ads}, the equilibrium constant for the adsorption process. Plots of $\log\left(\frac{[Clin]}{\theta}\right)$ against log [Clin] at different H_2SO_4 concentrations and different temperatures gave straight lines with intercepts equal to $-\log K_{ads}^{o}$ and slopes which should be ideally unity. Values of K_{ads}^{o} are then evaluated from the intercepts.

K_{ads} is related to the standard free energy of adsorption by Equation (8a)[11]:

$$K_{ads} = \frac{1}{55.5} e^{\left[\frac{-\Delta G_{ads}^{o}}{RT}\right]} \tag{8a}$$

Which can also be expressed as:

$$\Delta G_{ads} = -RT \ln(55.5\, K_{ads}^{o}) \tag{8b}$$

55.5 is the value of the molar concentration (M) of water in the solution[12].

The adsorption of dirithromycin on zinc can be better explained using the enthalpy and entropy of adsorption, which can be calculated from the integrated Van’t Hoff equation[13,14]:

$$\ln K_{ads} = \frac{-\Delta H_{ads}^{o}}{RT} + \frac{\Delta S_{ads}^{o}}{R} + \ln \frac{1}{55.5} \tag{9}$$

A plot of In K_{ads} against $\frac{1}{T}$ gave a straight line with slope equal to $\frac{-\Delta H_{ads}^{o}}{R}$ and intercept equal to $\frac{\Delta S_{ads}^{o}}{R} + \ln\frac{1}{55.5}$. ΔG_{ads} values at different temperatures were calculated using the basic thermodynamic equation

$$\Delta G_{ads}^{o} = \Delta H_{ads}^{o} + T\Delta S_{ads}^{o} \tag{10}$$

Inhibition efficiency

IE % values were simply calculated using Equation (11):

$$\text{IE \%} = 100\theta \tag{11),}$$

Where θ is the fractional surface coverage. IE% values were shown to be dependent of the concentrations of dirithromycin and H_2SO_4, and on temperature.

Arrhenius parameters

The effect of temperature on corrosion rates were analyzed using plots emanating from the Arrhenius-like equation:

$$\nu_{corr} = A.e\frac{-E_a}{RT} \qquad (12a)$$

which could be rewritten as:

$$\ln(\nu_{corr}) = \ln A - \frac{E_a}{RT} \qquad (12b)$$

A plot of $\ln(\nu_{corr})$ against $\frac{1}{T}$ gives a straight line, from which E_a and the A can both be determined from slope and intercept respectively.

Thermodynamics

The transition-state theory is an alternative to the Arrhenius theory, but with an advantage: it has been successful in calculating the standard enthalpy of activation ($\Delta H^{\ddagger}$), the standard entropy of activation ($\Delta S^{\ddagger}$) and the standard Gibbs energy of activation ($\Delta G^{\ddagger}$) for a particular reaction if its rate constant has been experimentally determined. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the formation of the activation complex were determining using Equation 13 (The transition-state equation):

$$\nu_{corr} = \frac{RT}{Nh} e^{\left(\frac{\Delta S^{\ddagger}}{R}\right)} e^{\left(-\frac{\Delta H^{\ddagger}}{RT}\right)} \qquad (13a)$$

which could be rewritten as:

$$\ln\frac{\nu_{corr}}{T} = \ln\frac{R}{Nh} + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT} \qquad (13b)$$

where h is Planck’s constant and N, the Avogadro’s number.

A plot of $\left(\ln\frac{\nu_{corr}}{T}\right)$ against $\frac{1}{T}$ gave a straight line with slope $-\frac{\Delta H^{\ddagger}}{R}$ and intercept $(\ln\frac{R}{Nh} + \frac{\Delta S^{\ddagger}}{R})$.

Results and Discussion

Adsorption isotherm and adsorption parameters

Adsorption is the process through which a substance, originally present in one phase, is removed from that phase by accumulation at the interface between that phase and a separate (solid) phase. The driving force for adsorption is the reduction in the interfacial tension between the fluid and the solid adsorbent as a result of the adsorption of the adsorbate on the surface of the solid.

The adsorption process is influenced by the chemical structures of organic compounds, charge distribution in the adsorbate molecules, the nature and surface charge of the metal and the type of corrodent[15-17]. The values of surface coverage for the different concentrations of dirithromycin were used to explain the best adsorption isotherm to describe the adsorption process. It was found that the isotherms for the zinc-dirithromycin system could be described by the classical Langmuir equation in the entire concentration and temperature ranges of the experimental data. Figure 2 shows the results of fitting using Langmuir isotherm equation. The linearity of the plots in Figure 2 implies that adsorption process is in conformity with the Langmuir isotherm. However, the slopes of the plots are not unity and this suggests the lack of perfect conformity with the isotherm. K^{o}_{ads} is a measure of how strongly the dirithromycin molecules are adhered onto zinc surface. As the temperature is increased, K^{o}_{ads} values become smaller, implying that high temperature shifts the adsorption-desorption equilibrium to favour desorption. However, K^{o}_{ads} values decrease with increasing H_2SO_4 concentration. The presence of the acid competes with dirithromycin for the zinc surface. Again, at a high acid concentration, a reaction between dirithromycin and the acid cannot be ruled out. ΔH^{o}_{ads} and ΔS^{o}_{ads} **v**alues in Table 1 are negative. Adsorption of dirithromycin leads to a decrease in the residual forces on zinc surface (as a result of the attractive forces between clindamycin molecules and zinc surface). This causes a decrease in the surface energy of the adsorbent, thereby making the process exothermic. Also, adsorption leads to a restriction of movement and decrease in disorderliness, i.e., lowering of entropy. There are marginal decreases in ΔH^{o}_{ads} and ΔS^{o}_{ads} values as the acid's concentration increases, implying that the adsorbent-adsorbate attraction reduces at high acid concentrations.

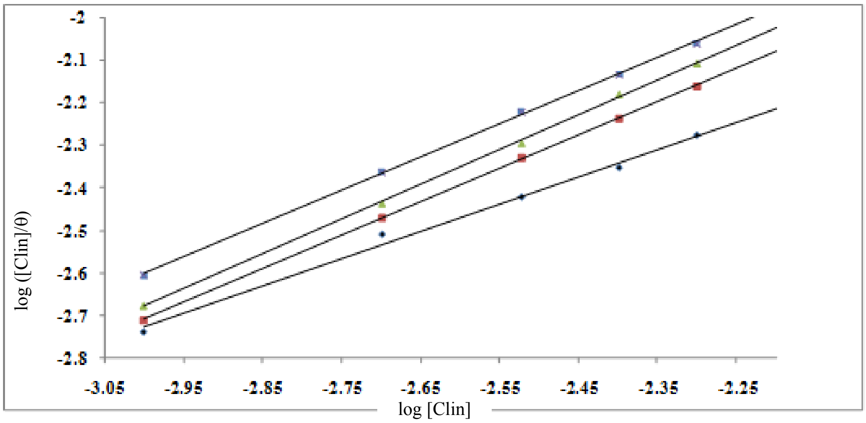

Figure 2. Langmuir isotherms for the adsorption of clindamycin on zinc surface at 303 K and different concentrations of H_2SO_4: a, b, c, d = 0.01, 0.02, 0.03, 0.04 M respectively.

The negative sign of ΔG^{o}_{ads} (Table 1) indicates a spontaneous interaction between dirithromycin molecules and zinc surface[18-20] and the stability of the adsorbed species on zinc surface. Values of ΔG^{o}_{ads} are lower than -15 kJ mol^{-1}; usually values of ΔG_{ads} around -20 kJ mol^{-1} or lower, are indicative of physisorption, while those higher than -40 kJ mol^{-1} involve chemisorption[21]. Values of $-\Delta G^{o}_{ads}$ (just like K^{o}_{ads}) decrease with increase in temperature (Table 1), implying that desorption is favoured at high temperature. Table 1 shows that there is an agreement between the values of ΔG^{o}_{ads} obtained via two different treatments, attesting to the validity of these results.

Table 1. Adsorption parameters determined from Langmuir and Van’t Hoff treatment of data

T, K	ΔH^{o}_{ads} /M^{-1}	ΔH^{o}_{ads} /kJ mol^{-1}	ΔS^{o}_{ads} /J mol^{-1} K^{-1}	* ΔG^{o}_{ads} /kJ mol^{-1}
0.01 M H_2SO_4				
303	6.33	-35.56	-68.47	-14.81 (-14.77)
313	4.26			-14.13 (-14.10)
323	2.64			-13.44 (-13.56)
0.02 M H_2SO_4				
303	4.23	-34.55	-68.21	-13.89 (-13.13)
313	3.22			-13.20 (-12.93)
323	1.80			-12.52 (-12.30)
0.03 M H_2SO_4				
303	2.71	-33.52	-68.19	-12.74 (-12.15)
313	2.02			-12.05 (-11.86)
323	1.18			-11.37 (-11.25)
0.04 M H_2SO_4				
303	1.81	-30.68	-62.54	-11.73 (-11.61)
313	1.42			-11.10 (-10.71)
323	1.05			-10.48 (-10.46)

**Values obtained using Equation 10; values in parentheses obtained using Equation 8*

Kinetic studies

The kinetics of the corrosion process was studied in order to determine the apparent corrosion rate constant as well as the order of the reaction with respect to H_2SO_4, using the differential method. The differential method involves measuring the corrosion rates at different H_2SO_4 concentrations. The rate of the reaction, ν, is represented as:

$$\nu = k' [H^+]^n \tag{14}$$

where k′ (= k [Zn]) is the apparent rate constant, and n the order of the reaction with respect to H^+. The corrosion rates were then plotted against H_2SO_4 concentration in accordance with Equation 15 (Figure 3),

$$\log n = \log k' + n \log [H^+] \tag{15}$$

As shown in Figure 3, the corrosion reaction is first order (n ~ 1) with respect to H^+.

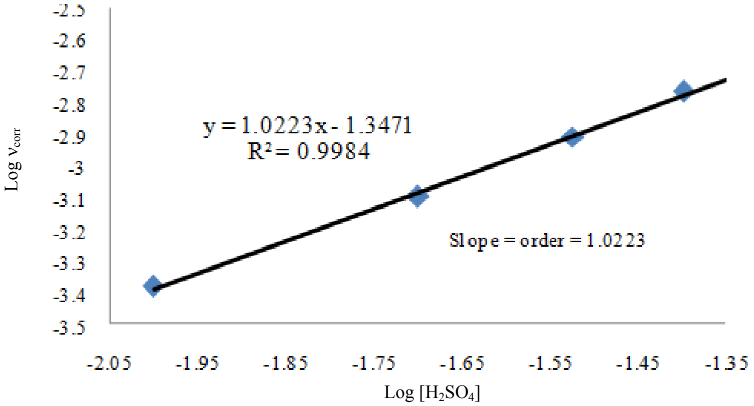

Figure 3. Determination of corrosion reaction order using the differential method

Effects of H_2SO_4 and dirithromycin concentrations on zinc corrosion

Corrosion rate increases steadily with the acid's concentration at the three temperatures under which the study was made (Table 2). This observation is readily explained in terms of the collision theory of reaction rates. For corrosion to occur at all, the zinc atoms and H_2SO_4 molecules must at least collide. A basic requirement in a corrosion cell is that the anode (metal, zinc) and the cathode (H^+) must be in electrical contact. If the concentration H_2SO_4 is higher, the chances of collision are greater, and an attendant increase in collision rate is expected.

Corrosion rate decreases at dirithromycin's (inhibitor) concentration increases (Table 2). A common mechanism for corrosion inhibition involves the formation of a coating, often a passivation layer, which prevents access of the corrosive substance (H_2SO_4 in this case) to the metal.

Table 2. Effects of dirithromycin concentration and temperature on the corrosion of zinc in H_2SO_4

	Corrosion Rate, x10^{-4} g cm^{-2} h^{-1}				Inhibition efficiency, %			
[H_2SO_4]	0.01	0.02	0.03	0.04	0.01	0.02	0.03	0.04
[Diri] (M); 303 K								
0	4.13	7.98	12.4	17.1	0	0	0	0
0.001	1.87	3.87	6.55	10.2	54.7	51.5	47.5	40.4
0.002	1.47	3.27	5.65	9.21	64.5	59.0	54.4	46.1
0.003	0. 85	2.85	5.09	8.56	79.4	64.2	59.0	49.9
0.004	0. 42	2.47	4.90	7.81	89.7	69.1	60.5	54.3
0.005	0. 22	2.20	4.44	7.27	94.7	72.4	64.2	57.5
[Diri] (M); 313 K								
0	7.82	14.7	21.3	28.8	0	0	0	0
0.001	4.39	8.61	13.0	18.1	43.9	41.4	39.1	37.2
0.002	3.80	7.83	12.3	17.1	51.4	46.7	42.2	40.7
0.003	3.21	6.91	11.1	16.0	59.0	53.0	47.8	44.3
0.004	2.80	6.21	10.4	14.7	64.2	57.7	51.4	49.8
0.005	2.30	4.90	9.00	14.2	70.6	66.7	57.8	50.6
[Diri] (M); 323 K								
0	15.8	29.7	43.7	58.1	0	0	0	0
0.001	9.50	18.2	27.7	38.8	39.8	38.5	36.7	33.3
0.002	8.72	17.5	26.7	36.6	44.7	40.9	38.9	37.0
0.003	7.82	16.2	25.8	35.4	50.4	45.3	40.9	39.0
0.004	6.65	14.8	24.3	33.3	57.9	50.3	44.4	42.7
0.005	6.04	12.9	21.9	32.0	61.7	56.6	49.9	44.9

However, Inhibition efficiency (I.E) increases on increasing the dirithromycin's concentration (Figure 4). Inhibition efficiency (I.E) was observed to decrease as the corrodent's concentration increases. At high H^+ concentrations, the corrosion rate is so high that the effectiveness of the inhibitor will be minimized. Again at a high concentration, H_2SO_4 probably attacks dirithromycin, thereby reducing the effective concentration of the inhibitor.

The effect of temperature on the acid-induced corrosion of a metal is rather complex; processes such as metal etching, alteration of the inhibitor adsorption-desorption equilibrium and the reaction (*e.g.*, decomposition) of the inhibitor itself[22], are bound to take place.

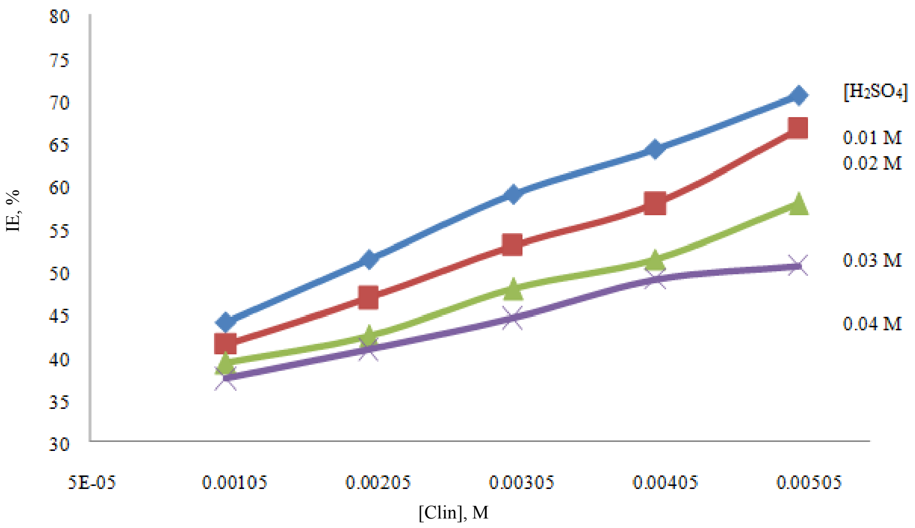

Figure 4a. Dependence of inhibition efficiency (I.E) on clindamycin and H_2SO_4 concentrations at 313 K

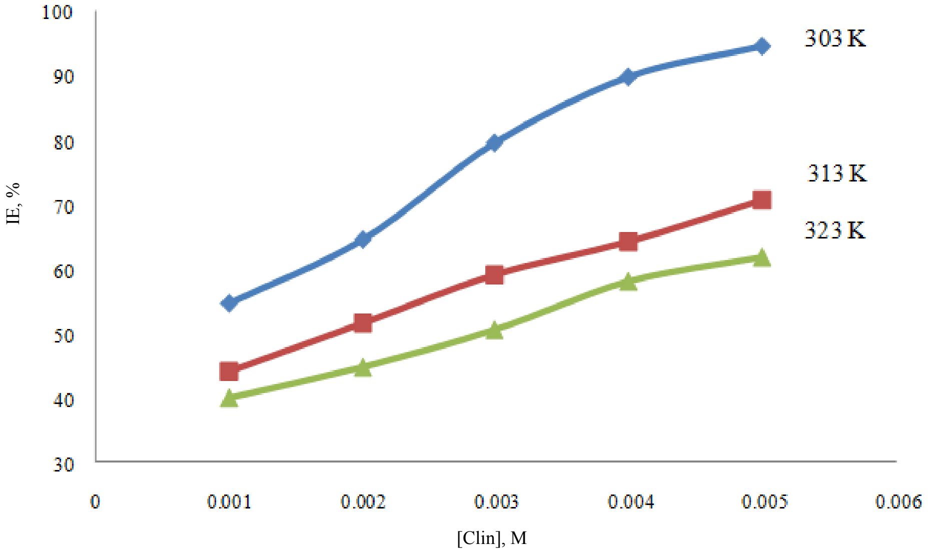

Figure 4b. Dependence of inhibition efficiency on temperature (H_2SO_4 concentration = 0.01 M)

Effects of temperature

For corrosion to take place, zinc atoms and H^+ ions must possess energies equal to or higher than the activation energy E_a. At low temperature, only a few molecules have sufficient energy - the reaction will proceed, but at a slow rate. At higher temperate, more molecules are able to surpass the energy barrier: the reaction proceeds at a faster rate.

At a particular H_2SO_4 concentration, corrosion rate increases with temperature (Table 2). Every reaction has an energy barrier. The fact that a reaction increases with increasing temperature suggests that only molecules with sufficient energy are able to react. In the presence of dirithromycin (inhibitor), inhibition efficiency (I.E) decreases as the temperature is increased. An increase in temperature might stimulate larger metal surface kinetic energy, which leads to a decrease in the quantity of dirithromycin adsorbed. Adsorption is an exothermic process[23] and one would expect therefore that an increase in temperature should cause a decrease in adsorption. Also, the adsorption-desorption process is a dynamic equilibrium, favouring desorption at high temperatures[24], and as a result of dirithromycin desorption, a greater surface area of zinc is exposed to the aggressive acid environment, resulting in an increase in corrosion rate and an attendant reduction in I.E. The decreased adsorption at high temperature indicates that dirithromycin is physically adsorbed onto zinc surface[17,25].

Arrhenius plots

The dependence of the corrosion rate on temperature can be expressed by the Arrhenius equation and transition state equation. The Arrhenius equation (Equation 12) predicts that corrosion rate increases with the temperature and Ea and A may vary with temperature. Figure 5 shows Arrhenius plots for the temperature dependence of zinc corrosion rates in the absence and presence of dirithromycin. The calculated activation energies (Ea) and pre-exponential factors (A) at different concentrations of dirithromycin are listed in Table 3.

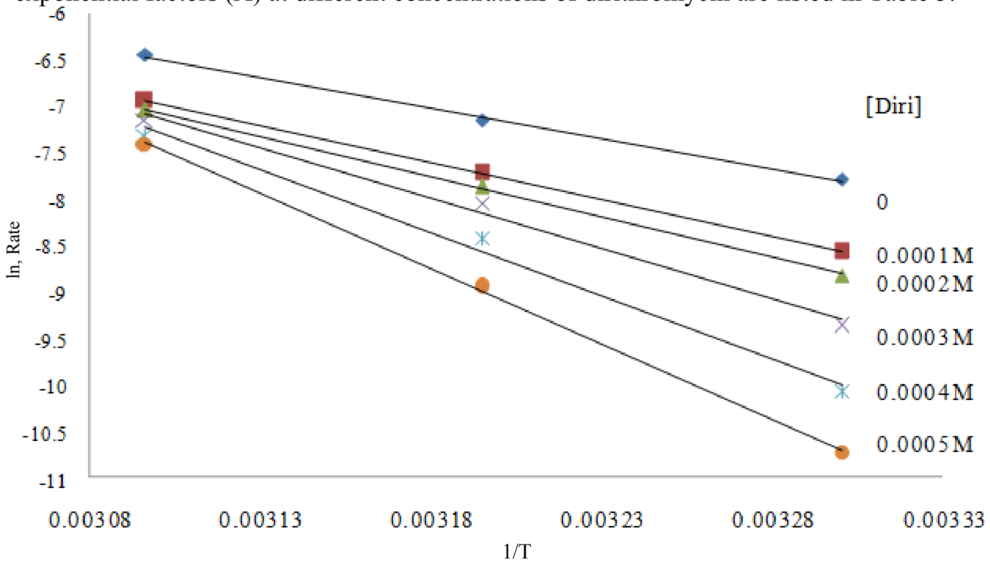

Figure 5. Arrhenius plots for the corrosion of zinc in H_2SO_4 - effect of clindamycin inhibitor

Both E_a and A increase as the concentration of dirithromycin is increased. The dirithromycin concentration-dependence of E_a may be explained thus: the adsorbed dirithromycin molecules modify the mechanism of the corrosion process by presenting an additional energy barrier for the process to take place[26,27]. At the molecular level, the H^+ ions do not have easy (direct) contact with the metal surface as the dirithromycin concentration is increased.

Activation thermodynamics

The activation parameters of the corrosion process in the presence of varying concentrations of dirithromycin are listed in Table 3. The activation enthalpy ($\Delta H^{\ddagger}$) is the least amount of energy required for a reaction to take place. It is the heat energy needed to raise the reactants to the transition state $\Delta H^{\ddagger}$ increases (becomes more positive) as dirithromycin concentration is increased. As explained above, the introduction of dirithromycin presents additional energy barrier for the process. The increase in $\Delta H^{\ddagger}$ reduces the tendency of $\Delta G^{\ddagger}$ to be negative ($\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$). So as expected, the presence of dirithromycin increases $\Delta H^{\ddagger}$, and therefore makes $\Delta G^{\ddagger}$ less negative (corrosion becomes less likely). $\Delta H^{\ddagger}$ varies with dirithromycin concentration in the same way as E_a (Figure 6). This observation permits us to verify the known thermodynamic relation between the two quantities for reactions in solution[28]:

$$E_a - \Delta H^{\ddagger} = RT \qquad (16)$$

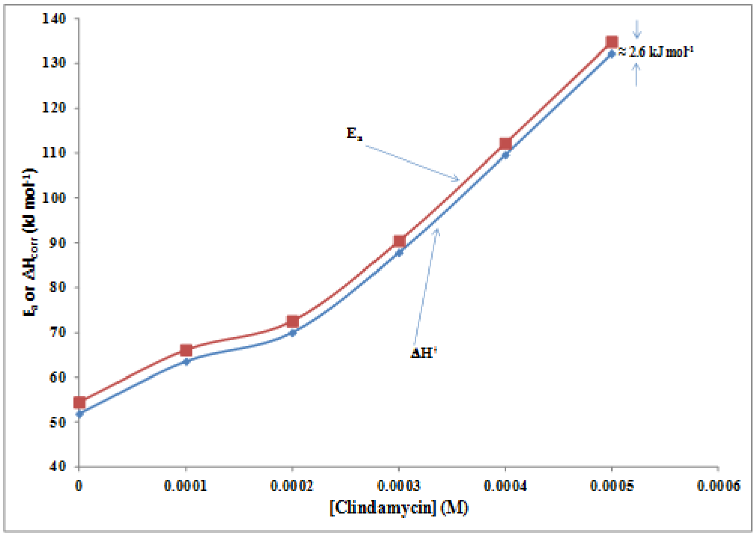

Figure 6. Variation of E_a and $\Delta H^{\ddagger}$ with clindamycin concentration; relationship between E_a and $\Delta H^{\ddagger}$

Table 3. Activation parameters for the corrosion of zinc in 0.01M H_2SO_4; effect of dirithromycin

[Diri] /M	E_a /kJ mol^{-1}	A /g cm^{-2} hr^{-1}	$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ /J K^{-1} mol^{-1}	E_a - $\Delta H^{\ddagger}$ /kJ mol^{-1}	$\Delta G^{\ddagger}$ at 303 K /kJ mol^{-1}
0	54.5	1.01×10^{6}	51.9	-82.0	2.598	+76.8
0.0001	66.1	4.66×10^{7}	63.5	-50.1	2.597	+78.7
0.0002	72.5	4.76×10^{8}	70.0	-30.8	2.593	+79.3
0.0003	90.4	3.47×10^{11}	87.8	24.0	2.588	+80.5
0.0004	112	9.98×10^{14}	109	90.2	2.587	+82.3
0.0005	134	3.94×10^{18}	132	159	2.595	+84.0

At 303, 313 and 323 K, the respective values of RT are 2.519, 2.602 and 2.685 kJ mol^{-1}, with an average of 2.602 J mol^{-1}. The values of $E_a - \Delta H^{\ddagger}$ at the different dirithromycin concentrations are listed in Table 3; these values are similar to 2.602 J mol^{-1} (within experimental error). This result shows that the inhibitor acted equally on E_a and $\Delta H^{\ddagger}$ (Figure 6). The difference between Arrhenius activation energy E_a and the activation enthalpy $\Delta H^{\ddagger}$ are quite small and numerically close to the accuracy attained in most experiments (RT = 2.5 kJ/mol at 298.15K). These two energies are therefore frequently used interchangeably in the literature to define the activation barrier of a reaction.

The activation entropy deals with how the energy within the molecule must be redistributed for the reaction to occur. For the uninhibited reaction, $\Delta S^{\ddagger}$ is negative (Table 3), suggesting that the activated complex in the rate-determining step represents an association rather than a dissociation step, which in turn implies that a increase in order takes place on going from reactants to the activated complex. It is logical to think that the presence of dirithroamycin molecules somewhat impedes the approach of the acid molecules unto the metal surface (thereby increasing disorder) in forming the activated complex. In Table 3, the value of $\Delta S^{\ddagger}$ increases (becomes more positive) with dirithromycin concentration, attaining 159 J mol^{-1} K^{-1} when [dirithromycin] = 0.0005 M.

The calculated $\Delta G^{\ddagger}$ values for the corrosion processes (Table 3) are positive, but increased in the presence of dirithromycin, suggesting that the activated complex is rather unstable, and the likelihood of its formation decreased marginally in the presence of dirithromycin (0.0001 – 0.0005 M). However, there are no marked changes in $\Delta G^{\ddagger}$ values as the temperature was increased to 313 and 323 K respectively.

Conclusion

In conclusion, this work has shown that dirithromycin, an antibacterial drug, suffices well for the inhibition of zinc corrosion in acid medim. The isotherms for the zinc-dirithromycin system could be described by the classical Langmuir equation in the entire concentration and temperature ranges of the experimental data; and decreased adsorption at high temperature indicates that dirithromycin is physically adsorbed onto zinc surface. The corrosion reaction was first order (n ~ 1) with respect to H^+, and was significantly inhibited by dirithromycin. The presence of dirithromycin increased $\Delta H^{\ddagger}$, and therefore made $\Delta G^{\ddagger}$ less negative (corrosion becomes less likely). $\Delta H^{\ddagger}$ varied with dirithromycin concentration in the same way as E_a. The calculated $\Delta G^{\ddagger}$ values for the corrosion processes were positive, but increased in the presence of dirithromycin, suggesting that the activated complex was rather unstable.

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