Inhibition of corrosion of zinc in 0.1m H₂So₄ by 5-amino-1-cyclopropyl-7-[(3r,5s)3,5-dimethylpiperazin-1-yl]-6,8-difluoro-4-oxo-quinoline-3-carboxylic acid (A)

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ABSTRACT

Effect of A on the corrosion of zinc has been studied by using weight loss and gasometric methods. The study revealed that A inhibits the corrosion of zinc with corrosion efficiency ranging from 34.64-73.50%. The kinetics of uninhibited and inhibited corrosion reaction of zinc is found to be first order. Values of rate constant and half-life ranged from 0.1076-1.10893 and 24-154days respectively. Average values of activation energy (E_a) of the inhibited corrosion reaction (5.1751J/mol) was higher than average values of activation energy obtained for the uninhibited corrosion reaction(-13.0760J/mol). Average values of enthalpy change(ΔH_{ads} =-15.1751J/mol) and entropy change (ΔS_{ads}=-279.8631J/mol) and free energy of adsorption (ΔG_{ads}= -87.5829KJ/mol) reveal that the inhibited corrosion reaction of zinc is spontaneous and exothermic. From the calculated thermodynamic parameters the inhibited corrosion reaction of zinc is controlled by activation complex and proceeds via chemical adsorption. An adsorption characteristic of the studied inhibitor(A) is found to obey the classical isotherm of Lagmuir.
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INTRODUCTION

A corrosion inhibitor is a chemical substance that when applied in small quantities to corrosive medium reduces the rate of corrosion of a metal or a metal alloy[1-6]. A search for a suitable inhibitor for the corrosion of zinc (in acidic medium) involves a choice between those synthesised from cheap raw materials and those containing hetero-atoms (N,O,S or P) in aromatic or long chain carbon compound[4-6].

In addition to other uses, zinc is often used for electro- protection of iron against corrosion implying that a search for an inhibitor that can retard zinc corrosion should require adequate attention. The present study seeks to use 5-amino-1-cyclopropyl-7-[(3r,5s)3,5-dimethylpiperazin-1-yl]-6,8-difluoro-4-oxo-quinoline-3-carboxylic acid (A) to inhibit the corrosion of zinc in 0.01M H₂SO₄.

MATERIALS AND METHODS

Materials

The sample (A) was synthesized by chemical method as reported by Mandell et al.,[7]. Zinc specimens used for the study were of dimension of 5×4×0.11cm. The acid solutions (0.01 and 2.5M H_2SO_4) were prepared from analar grade. The zinc coupon was washed in ethanol, dried in acetone and preserved in a dessicator. Various concentrations(1×10^{-4}-5×10^{-4}M) of A were also prepared.

Weight loss measurement

Weight loss measurements were carried out as described in literature[8-10]. The volume of acid used for the immersion test was 150ml. Zinc electrode was immersed in solutions of acid and inhibitors (dissolved in 0.01M H_2SO_4). Each set of experiment was conducted under thermostated condition (303, 313 and 323K). Prior to weight loss measurement, each coupon was withdrawn from their respective solution, washed in 5% chromic acid solution (containing 1% silver nitrate, in 10% aluminum chloride), rinsed in boiling water and dried in acetone before weighing .

From weight loss measurement, inhibition efficiency and degree of surface coverage were calculated using equation 1 and 2 respectively[2-5].

$$\%I=(1-W_1/W_2)\times100 \tag{1}$$
$$\theta== 1 - W_1/W_2 \tag{2}$$

where W_1 and W_2 are the weight losses (g/dm³) for mild steel in the presence and absence of inhibitor in H_2SO_4 respectively.

Gasometric method

Gasometric method was carried out as described in literature[11-13] From the volume of hydrogen evolved per minutes, inhibition efficiency of A was calculated using equation 3

$$I(\%)=\{1- V'_{Ht}/ V^0_{Ht}\}\times100 \tag{3}$$

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 unhibited solution

RESULTS AND DISCUSSION

Effect of concentration and temperature

Figure 1 shows weight loss of zinc in 0.01M H_2SO_4 in the presence of 0.0001-0.0005M of A as additive. Comparing figure 1 with figure 1b(inserted in figure 1), it can be seen that values obtained for weight losses of

zinc in the presence of different concentrations of A were generally lower than values obtained for the blank (figure1b) indicating that A retard the corrosion of zinc.

Weight losses were observed to increase with temperature indicating that corrosion rate of zinc is lowered at higher temperature and that A is adsorbed on zinc electrode by chemical adsorption[14-15].

Kinetics and thermodynamics considerations

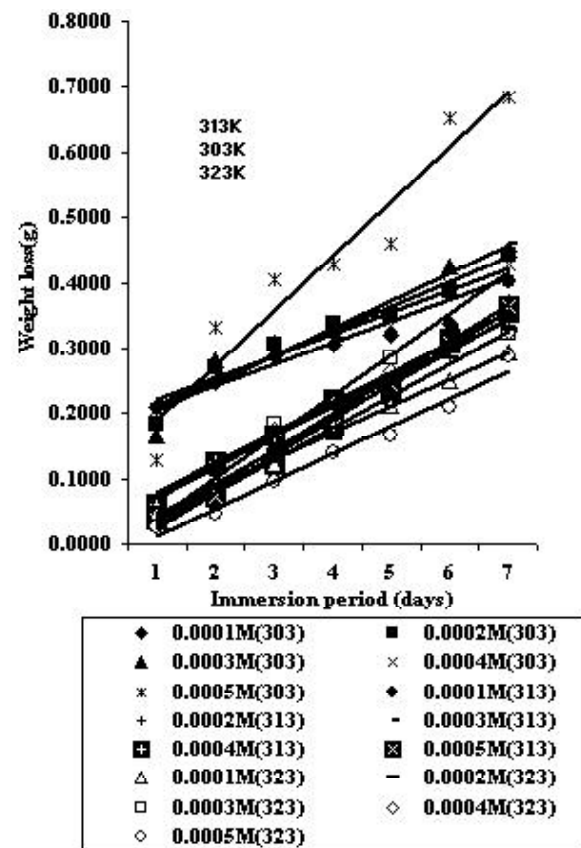In order to determine the order of the uninhibited

Figure 1: Weight loss of zinc in 0.1M tetraoxosulphate (VI) acid in the presence of A
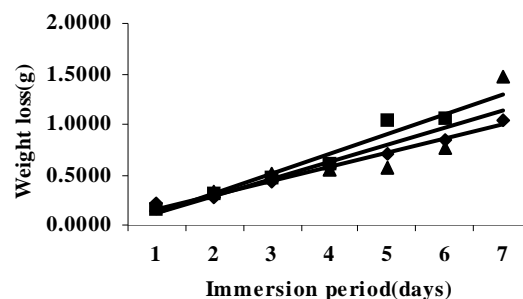

Figure 1(b): Weight loss of zinc(blank)

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and inhibited corrosion reaction of zinc, Attempts were made to fit data obtained from weight loss measurements with respect to zero, first and second orders. By far the uninhibited and inhibited corrosion reactions of zinc were found to obey first order kinetics at all temperatures. A first order equation can be written as equation (4)[16]:

$$-d(a_o-x)/dt = K_1 t \qquad (4)$$

where a_o-x is the weight loss of zinc electrode, K_1 is the first order reaction rate constant and t is the time in days.

Rearranging and integrating equation 4, equation 5 is obtained:

$$-Log((a_o-x)/a_o = K_1 t/2.303 \qquad (5)$$

From equation 5, a plot of -Log[weight loss of mild steel] versus time should produce a straight line with slope equals to $K_1/2.303$. The half lives of the inhibited and uninhibited corrosion reactions were also calculated using equation 6[16-17]:

$$t_{1/2} = 0.693/K_1 \qquad (6)$$

Figure 2 shows kinetic plot for the corrosion of zinc in 0.01M H_2SO_4 in the presence of different concentrations of A. From slopes of lines on figure 2, values of K_1 were calculated. Values of $t_{1/2}$ were also calculated by substituting K_1 values into equation 6. From calculated values of $t_{1/2}$, it is found that A has the tendency of extending the half life of zinc corrosion.

In order to calculate the activation energy of the corrosion reaction of zinc in 0.01M H_2SO_4, the Arrhenius equation was used (equation 7)[16-17].

$$K = exp(-E_a/RT) \qquad (7)$$

Where K is rate constant obtained from the slope of kinetic plots (Figure 2), E_a is the activation energy of corrosion, R is the gas constant and T is the temperature. Transforming equation 6 to logarithm form, equation 8 is obtained:

$$LogK = -E_a/2.303RT \qquad (8)$$

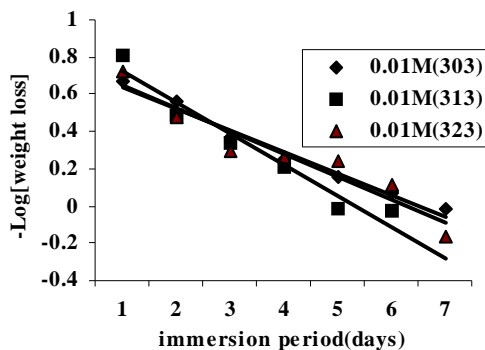From equation 7, a plot of LogK versus 1/T should

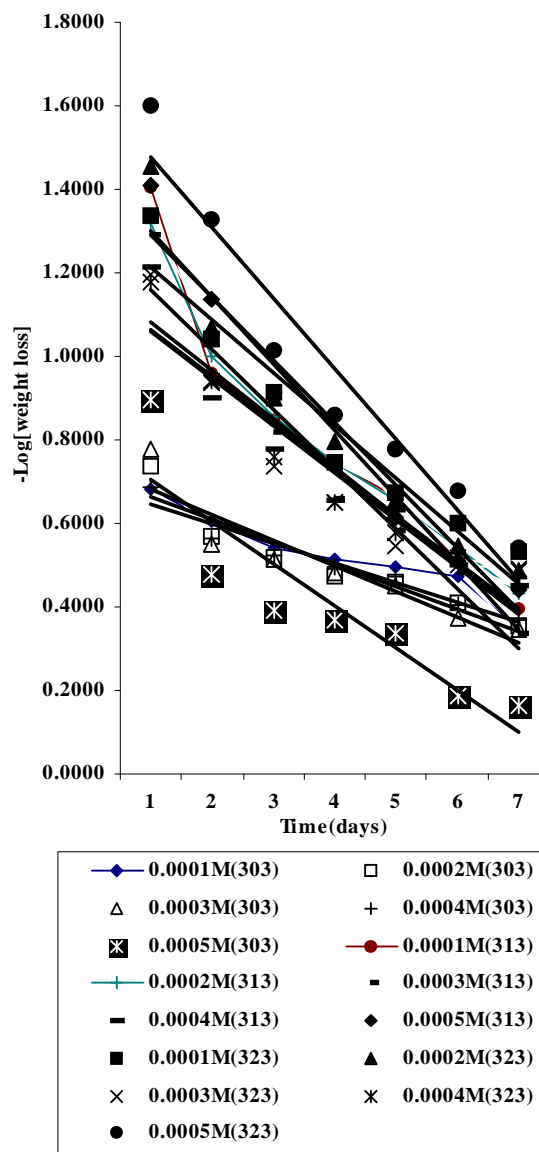**Figure 2a: Kinetic plot for corrosion of Zn in the blank**

Figure 2: Kinetic plot for the corrosion of Zn in 0.01M acid in the presence of A(insert, plot for the blank)

produce a straight line with slope equal to $-E_a/2.303R$.

TABLE 1: Values of rate constant and half-life (days) for corrosion of Zn in 0.01M H_2SO_4 in the presence of 0.0001-0.0005M(A)

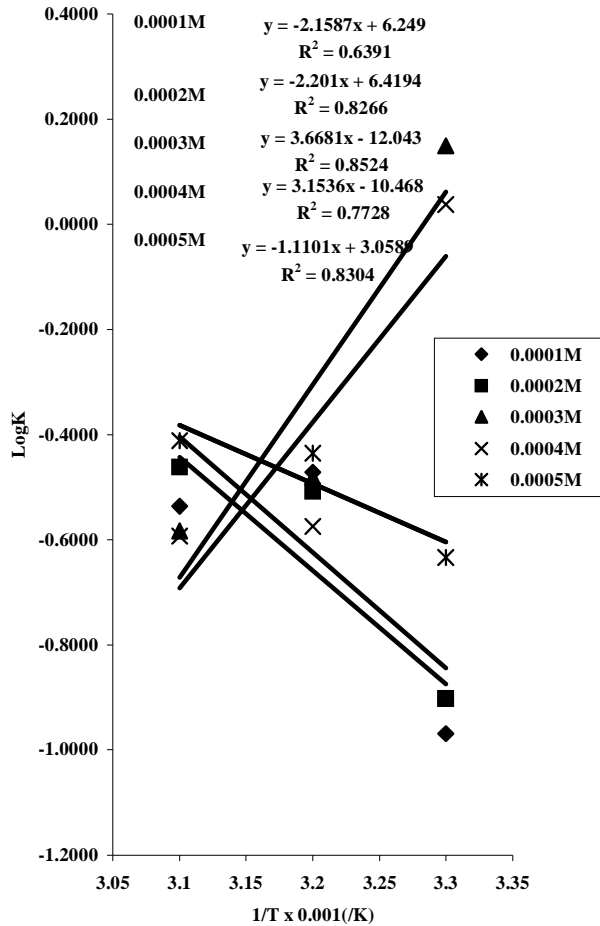| Con. mol/dm³	K_1(303)	K_1(313)	K_1(323)	$t_{1/2}$(303)	$t_{1/2}$(313)	$t_{1/2}$(323)
0.0001	0.1076	0.3376	0.2906	154	48	58
0.0002	0.1253	0.3109	0.3452	132	53	48
0.0003	1.4117	0.3300	0.2607	24	56	72
0.0004	1.0893	0.2665	0.2549	24	63	72
0.0005	0.2326	0.3669	0.3878	72	48	48

Figure 3: Arrhenius plot for corrosion of zinc in 0.01M acid corrosion in the presence of A
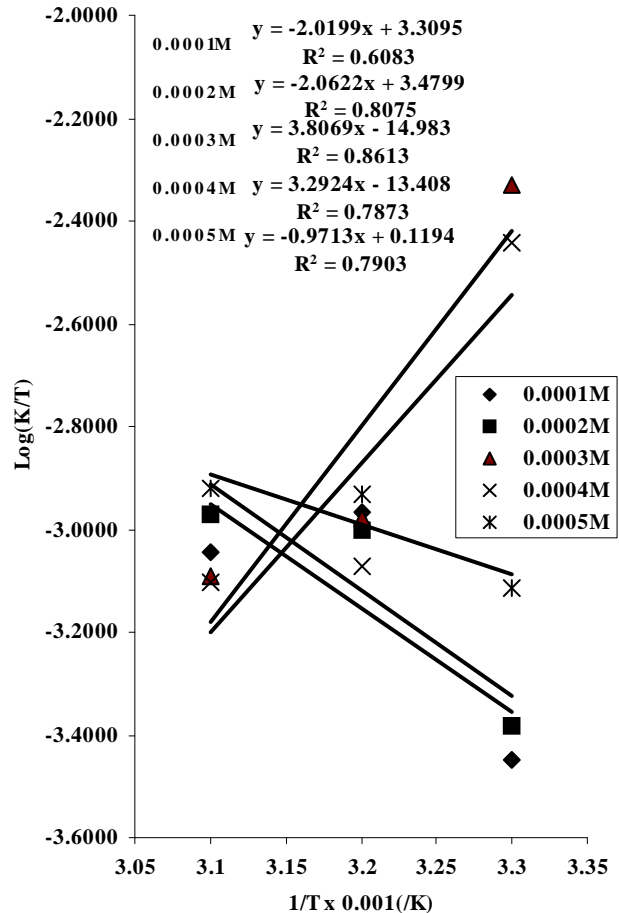

Figure 4: Transition state plot for the corrosion of zinc in 0.01M acid in the presence of A

TABLE 2: Thermodynamic parameters for the corrosion of zinc in 0.01 –0.01M H$_2$SO$_4$ in the presence of 0.0001-0.0005M (A)

Con. mol/dm^3	E_a(J/mol)	ΔH^o(J/mol)	ΔS^o(J/mol)	ΔG^o(303)(KJ/mol)	ΔG^o(313)(KJ/mol)	ΔG^o(323)(KJ/mol)
0.0001	-41.3329	38.6753	-134.2310	-40.7107	-42.0530	-43.3953
0.0002	-42.1429	39.4852	-130.9684	-39.7229	-41.0326	-42.3423
0.0003	70.2336	-72.8913	-484.4801	-146.7246	-151.5694	-156.4142
0.0004	60.3729	-63.0401	-454.3234	-137.5970	-142.1402	-146.6834
0.0005	-21.2552	-18.5976	-195.3123	-59.1610	-61.1142	-63.0673
Mean	5.1751	-15.2737	-279.8631	-84.7832	-87.5819	-90.3805

Figure 4 shows Arrhenius plot for the corrosion of zinc. From the slope of lines on the plots, calculated values of E$_a$ ranged from 21.2552-70.2336J/mol(mean = 5.1751J/mol)(TABLE 2) implying that the activation energy of the inhibited corrosion reaction of zinc is higher than that of uninhibited corrosion reaction of zinc(average E$_a$ = - 13.0760J/mol) and thatA inhibits the corrosion of zinc.

In order to calculate thermodynamic parameters for the corrosion reaction of zinc, transition state equation (equation 9) was used[16-17]:

K=RT/Nhexp(ΔS/R)exp(-ΔH/RT)   (9)

Rearranging and integrating equation 8, equation 9 is obtained.

Log(K/T)=LogR/Nh +ΔS/2.303R-ΔH/2.303RT   (10)

where N is Avogadro's number and h is the plank constant. From equation 9, a plot of LogK/T versus 1/T should produce a straight line with slope equal to -ΔH/2.303R and intercept equals to LogR/Nh + ΔS/2.303R

Values of ΔH$_{ads}$(TABLE 2) calculated from slopes of lines on the plot (Figure 3) ranged from -72.8913-39.4852J/mol(mean = -15.2737J/mol) indicating that

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the inhibited corrosion reaction is spontaneous. Values of ΔS_{ads} calculated from intercepts of lines on figure 3 ranged from -130.9684-484.4800J/mol(mean= -279.8631J/mol). The large and negative values of ΔS_{ads} obtained for the inhibited corrosion reaction of zinc indicates that adsorption of A on zinc surface is controlled by activation complex and that there is association instead of dissociation. .

Values of free energy of adsorption ΔG_{ads} were calculated by substituting values of ΔH_{ads} and ΔS_{ads} into equation 11[16].

$$\Delta G^o = -\Delta H^o - T\Delta S^o \qquad (11)$$

Mean values of ΔG_{ads} calculated from equation 10 ranged from –84.7832 - -90.3805J/mol These values are negative and are above the threshold value of 40KJ/mol required for physical adsorption therefore adsorption of A on zinc surface is spontaneous and proceeds via chemical adsorption[10-15].

Adsorption consideration

Adsorption isotherm provides a clue to the mode and mechanism of adsorption. Attempts were made to fit data obtained from weight loss measurement into different adsorption isotherm including those of Lagmuir, Frumkin, Freundlich, Temkin, Florry Huggins, and El awardy isotherms. By far the data fitted Lagmuir adsorption isotherm best.

Assumption of Lagmuir adsorption isotherm is expressed by equation 12[18-20]

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

where C is inhibitor's concentration, θ is the degree of surface coverage and K is the binding constant. From equation 11, a plot of C/θ versus C should give a straight line with intercept equals to 1/K. (Ashassin-sorkhabi et al., 2006). Lagmuir plot for the inhibited corrosion reaction is shown by figure 4. The fact that lines on the figures are linear and very close to each other (with R^2 ranging from 0.8538-0.9972) confirms that Lagmuir isotherm is obeyed and that the mechanism of adsorption is the same. The applicability of Lagmuir adsorption isotherm to the adsorption of A on zinc electrode suggests that there is a high increase in the free energy with respect to uninhibited system. The results show strong adsorption of inhibitors on the mild steel surface and the existence of monolayers of adsorption[18-20].

TABLE 3: Inhibition efficiency of A for the corrosion of Zn in 0.01M H_2SO_4

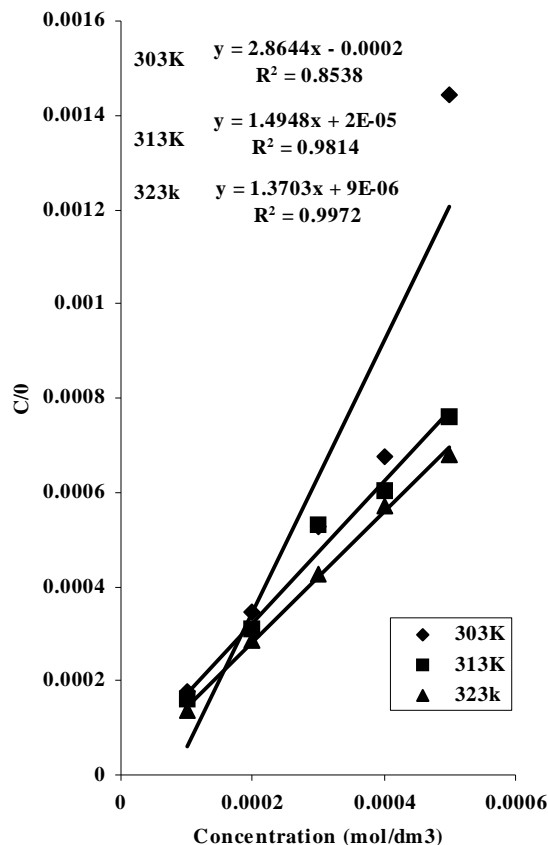| Con (mol/dm³)	Gasometric methods (2.5M H_2SO_4)	0.01M tetraoxosulphate (VI) acid(weight loss)		
		303K	313K	323K
0.0001	48.45	57.07	62.22	72.89
0.0002	48.40	57.66	64.97	69.8
0.0003	50.21	56.8	56.57	70.17
0.0004	52.32	59.27	66.42	70.09
0.0005	45.21	34.64	65.71	73.50

Figure 5: Curve fitting for adsorption of sparfloxacin on mild Zn according to Lagmuir

From the intercept of Lagmuir plot (Figure 4) calculated values of the binding constant, K at 303, 313 and 323K were 5000, 50000 and 111111.10 respectively. These values are large confirming that A is strongly adsorbed on zinc surface.

Inhibition efficiency of A

Values of inhibition efficiency of A calculated from weight loss measurement are recorded in TABLE 3. The result shows that Inhibition efficiency of A increases with temperature indicating chemical adsorption. Figure 6 shows a plot of variation of inhibition efficiency of
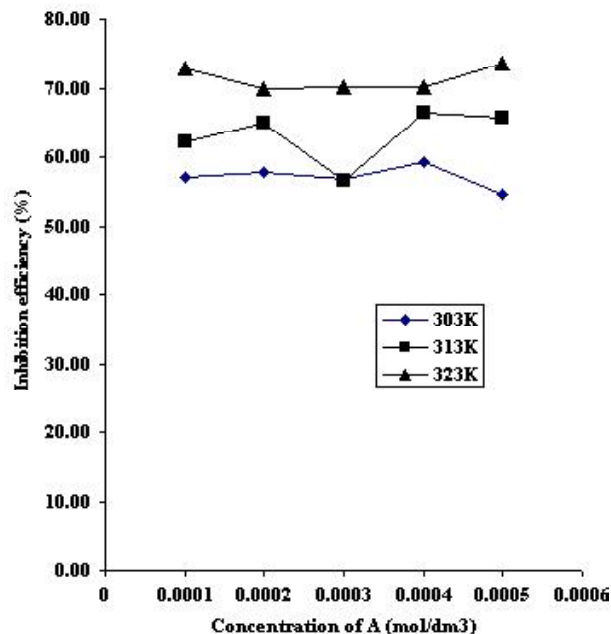
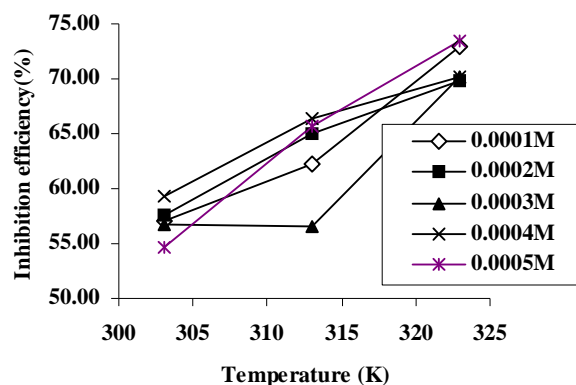**Figure 6(a): Variation of inhibition efficiency of A with concentration of A**

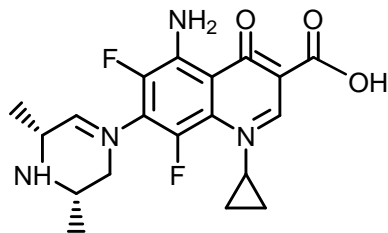**Figure 6b: variation of inhibition efficiency with temperature**

Figure 7: Chemical structure of A

A with concentration (Inserted, Figure 6a is the plot showing the variation of inhibition efficiency of different concentration of A with temperature). From the figures, it is obvious that inhibition efficiency of A shows slight variation with concentration but a proportional varia-

tion with temperature.

Values of inhibition efficiency of A obtained from gasometric method were higher than values obtained from weight loss method. This may be due to the fact that weight loss method measures average value inhibition efficiency while gasometric method measures instantaneous value of inhibition efficiency. However, there was a strong correlation between values obtained from both methods (r= 0.8288).

Mechanism of inhibition

The inhibitor used has a high molecular weight of 392.41g/mol and molecular formula, $C_{19}H_{22}F_2N_4O_3$. It contains heteroatoms (N, O) bonded to three aromatic rings (Structure I) Its high molecular mass and electron rich bonds/functional groups are factors that enhanced the inhibition action of A.. Based on its structure(Figure structure I), the following inhibition mechanism is proposed for the used inhibitor (A):

i.   In acidic medium, A undergoes dehydration to yield anhydrosparfloxacin which suffers further cleavages and lactorization

ii. Dilute acid promotes epimerization of C-bonds, therefore, we propose that adsorption of A on zinc surface hence its inhibition efficiency is stabilized by each molecule of A donating electron to a vacant orbital of iron.

iii. The proposed mechanism is supported by moderate values of activation energy (mean = 5.1751J/mol) and other thermodynamic parameters. The fairy high negative values of entropy (mean = -279.8631J/mol) of adsorption suggest the formation of a compact activated complex with fewer degree of freedom.

CONCLUSION

From the results of the study, the following conclusions are drawn, A is a good inhibitor for the corrosion of zinc in 0.01M H_2SO_4. Inhibition efficiency of A is dependent on concentration and temperature. Inhibited corrosion reaction of Zn in the presence of A is controlled by activation complex Adsorption of A on zinc surface is spontaneous and proceeds via chemical adsorption according to classical isotherm of Lagmuir.

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