Norfloxacin and sparfloxacin as corosion inhibitors: comparative study

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ABSTRACT

Effect of norfloxacin and sparfloxacin on the corrosion of zinc in 0.001-0.005M H_2SO_4 have been studied. Both compounds inhibit the corrosion of zinc in H_2SO_4 medium. Their inhibition efficiency is most affected by concentration of H_2SO_4 and temperature. A graduation in thermodynamic parameters of adsorption(ΔH_{ads}, ΔG_{ads}, and E_a)of norfloxacin and sparfloxacin was observed between H_2SO_4 concentration range of 0.01-0.03M and 0.03-0.05M respectively. Although activation energies of norfloxacin and sparfloxacin inhibited corrosion reaction of zinc were positive and greater than activation energy of uninhibited corrosion reaction of zinc, a significant statistical differences (P≤0.05) was observed between the values of E_a obtained for norfloxacin and sparfloxacin. Corrletaion between the two set of data was also weak. Values of ΔH_{ads} and ΔG_{ads} were negative for both inhibitor sand were also found to be significantly difference from each other.
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KEYWORDS

INTRODUCTION

In our laboratory, we have found that norfloxacin and sparfloxacin are good inhibitors for zinc corrosion. Inhibition efficiency of this compound has been attributed to the presence of heteroatoms in their electron rich aromatic chains[1-3]. In addition several factors affects inhibition inhibition efficiency of a given inhibitor including, temperature, presence or aggressive ions, concentration of corrodent, acidity(pH), concentration of inhibitors, etc.[4-7]. Our present study is aimed at investigating inhibitive action of norfloxacin and sparfloxacin in H_2SO_4 medium.

MATERIALS AND METHODS

Materials

The samples (norfloxacin and sparfloxacin) were synthesized by chemical method as reported by Ferrera et al.,[3]. Zinc specimens used for the study were of dimension, $5 \times 4 \times 0.11$cm. The acid solutions (H_2SO_4) were prepared from analar grade (manufactured by BDH chemicals). Double distilled water was used for all preparations. The concentration range of inhibito employed was 110^{-3}-5×10^{-3}M. These were separately dissolved in 0.01, 0.02, 0.03, 0.04 and 0.05M.

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Weight loss measurement

Weight loss measurements were carried out as described in literature[10-15]. The volume of solution used was 150ml. A maximum immersion time was 168hours. Solutions were not stirred but specimens were removed from their respective solution after every 24hours of immersion. They were washed in 5% chromic acid solution (containing 1% silver nitrate in 10% aluminum chloride solution), rinsed in boiling water and dried in acetone before weighing to the nearest 4 decimal place.

From weight loss measurement, inhibition efficiency and degree of surface coverage were calculated using equation 1 and 2[10-12]:

Inhibition efficiency(%)=$(1-W_1/W_2)\times100$ **(1)**

Degree of surface coverage(θ)=$(1-W_1/W_2)$ **(2)**

where W_1 and W_2 are weight losses (g/dm^3) of zinc in the presence and absence of A respectively.

RESULTS AND DISCUSSION

Effect of concentrations

Figure 1-2 show plots of weight loss versus immersion time for the corrosion of zinc in 0.01-0.05M H_2SO_4 in the presence of 0.0001-0.0005M norfloxacin and sparfloxacin at 303K. Figure 4 shows a plot of weight loss versus immersion time for the corrosion of zinc in 0.01 -0.05M H_2SO_4. weight losses of zinc in the presence and absence of the inhibitors are found to vary with the concentration of H_2SO_4 and temperature. However values of weight losses obtained in the absence of inhibitors are higher than values obtained in the presence of inhibitors indicating that these compounds in-
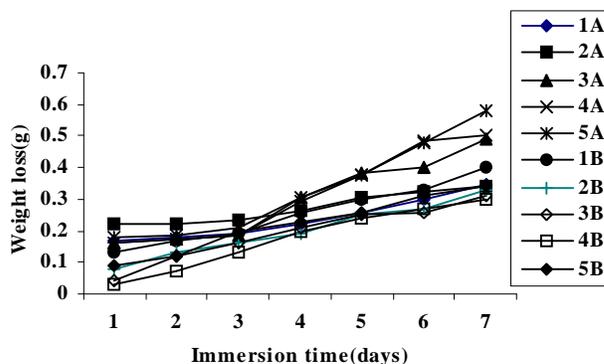
Figure1a: Variation of weight loss with immersion time for the corrosion of zinc in 0.01M(A) & 0.02M(B) acid in the presence of 0.0001-0.0005M norfloxacin
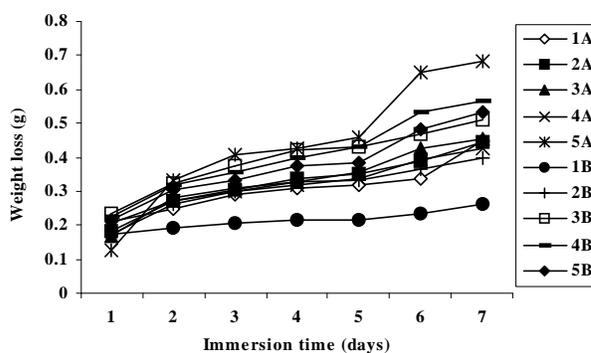
Figure 1: Weight loss versus immersion time for the corrosion of zin in 0.01M(A) & 0.02M(B) in the presence of 0.0001-0.0005M(1-5) sparfloxacin at 303K

hibit the corrosion of zinc. Lines on the respective plot were close and parallel to each other implying that they follow similar corrosion mechanism. In the presence of inhibitors, weight losses were found to decrease with inhibitors concentration (in most cases) indicating that inhibition efficiency of the used compounds decreases with concentration. At H_2SO_4 concentration ranges of
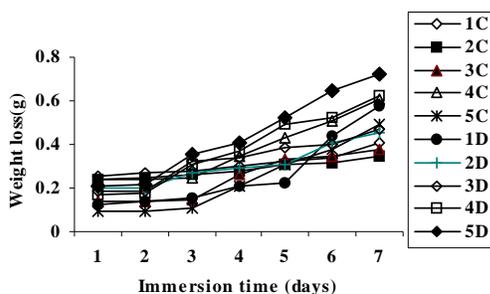
Figure 2a: A plot of weight loss versus immersion time for the corrosion of zinc in 0.03M(C) & 0.04M (D) in the presence of 0.0001-0.0005M(1-5) norfloxacin0.04M(D) in the presence of 0.0001-0.0005M(1-5) norfloxacin
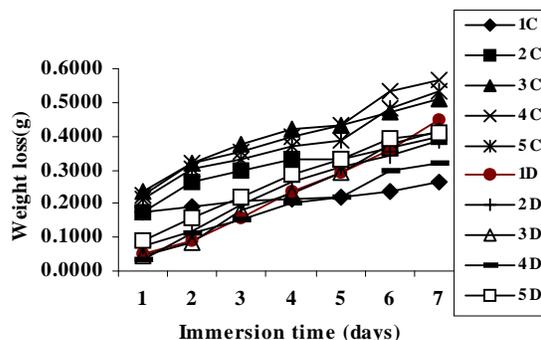
Figure 2: Variation of weight loss with immersiontime for the corrosion of zinc in 0.03M(C)& 0.04M(D) in the presence of 0.0001-0.0005M(1-5) of norfloxacin at 303K

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0.01-0.03M and 0.03-0.04M, were relatively afar from each other for norfloxacin and sparfloxacin respectively. At 313 and 323K, weight losses were also found to increase with immersion time and follows trend corresponding to the respective compounds at similar concentration and temperature of 303K.However, values of weight losses were generally low at these 313 and 323K indicating that inhibition efficiency of these compounds increases with temperature, a character common to chemical adsorption species.

Kinetics consideration

Corrosion reactions of zinc in 0.01-0.05M H_2SO_4 in the absence and presence of the two inhibitors were found to follow first order kinetics.indicating that the fraction of zinc that corrodes increases exponentially with time according to equation 3

$$[Zn]/[Zn]_o = -K_1 t \qquad (3)$$

Where $[Zn]_o$ and $[Zn]$ are the concentrations of zinc at time t=0 and at time, t. K_1 is the first order rate constant. Rearranging equation 3 4 is obtained:

$$-log\{[Zn] - [Zn]_0 = K_1 t/2.303 \qquad (4)$$

Plotting of Log[weight loss] versus time(Figures not shown) produces straight lines for both norfloxacin and sparfloxaxcin implying that first order kinetic is obey.. From slopes of the kinetic plots, values of K_1 calculated where used to calculate values of half life at different concentrations of norfloxacin and sparfloxacin (Values not indicated) using equation 5[10-12]:

$$t_{1/2} = 0.693/K_1 \qquad (5)$$

Calculated values of half life for inhibited corrosion reaction of zinc ranged from 54-150days and were higher than values obtained for the respective blank(which ranged from 0.678-1.5days) implying that norfloxacin and sparfloxacin extend the half life of zinc corrosion in H_2SO_4 medium.

Thermodynamics and adsorption considerations

In order to study the effect of temperature on the corrosion reaction of zinc in H_2SO_4 in the presence and absence of sparfloxacin and norfloxacin, Arrhenius equation was used [4-9]:

$$K = Aexp(-E_a/RT) \qquad (6)$$

where K is the rate constant obtained fom equation 4, A is Arrhenius or pre-exponential constant, E_a is the activation energy, R is the gas constant and T is the temperature.

Taking logarithm of both sides of equation 6, equation 7 is obtained:

$$LogK = LogA + E_a/2.303RT \qquad (7)$$

Plotting of respective values of K for norfloxacin and sparfloxacin yielded straight lines representing Arrhemius plot for the respective inhibitor at different temperatures. From slopes of lines on each plot, values of E_a were calculated. Calculated values of E_a (TABLE 1) for inhibited corrosion reactions of zinc in the presence of sparfloxacin and norfloxacin were positive and

TABLE 1: Values of thermodynamic parameters for the adsorption of norfloxacin and sparfloxacin on zinc surface

Activation energy			Thermodynamic parameters of norfloxacin			
Con. (M) of inhibitor	Ea(J/mol) 0.02M H_2SO_4		Con.(M) of acid	T(K)	ΔG_{ads} (KJ/mol)	ΔH_{ads} (J/mol)
	Sparf	Norf				
				303	33.3260	
0.001	-41.3329	43.6229	0.01	313	41.4361	-34.0520
0.002	-42.1429	71.3557		323	39.3930	
0.003	70.2336	16.951		303	34.2250	
0.004	60.3729	136.2511	0.02	313	36.3595	-39.9700
0.005	-21.2552	6.8221		323	43.1827	
0.02M H_2SO_4				303	35.6347	
0.001	33.4692	69.2227	0.03	313	40.0263	-36.4110
0.002	-5.3803	61.9238		323	43.1827	
0.003	46.3667	16.0721		303	16.4855	
0.004	33.6875	6.8604	0.04	313	14.4897	-16.8420
0.005	24.2767	-5.2176		323	15.4960	
0.03M H_2SO_4				303	24.9756	
0.001	68.8838	39.7188	0.05	313	19.3348	-25.5190
0.002	58.9866	-86.8036		323	14.5098	
0.003	33.5554	51.5575	**Thermodynamic parameters of sparfloxacin**			
0.004	24.9736	49.6658		T (K)	ΔG_{ads}(KJ/mol)	ΔH_{ads} (J/mol)
0.005	23.5031	43.2917		303	31.5795	
0.04M H_2SO_4			0.01	313	37.3811	-88.6850
0.001	75.074	18.9269		323	39.3930	
0.002	45.6506	19.7905		303	34.6131	
0.003	47.2571	8.239	0.02	313	40.0263	-70.2550
0.004	30.5952	19.9571		323	41.4363	
0.005	34.9474	4.5226		303	35.6347	
0.05M H_2SO_4			0.03	313	36.3595	-17.6590
0.001	29.1802	-6.3779		323	39.1276	
0.002	28.1731	-24.5581		303	37.3811	
0.003	42.4492	-23.1106	0.04	313	47.9627	-24.578
0.004	27.1066	-12.6141		323	41.4363	
0.005	20.2672	79.0854		303	37.3811	
			0.05	313	37.3811	-38.1950
				323	37.3811	

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higher than values obtained for the respective blank implying that nofloxacing and sparfloxacin retards the corrosion of zinc in H_2SO_4. However, values obtained for norfloxacin(at H_2SO_4 concentration of 0.01 and 0.02M) were greater and significantly difference from values obtained for norfloxacin (P=0.05). At H_2SO_4 concentrations of 0.03, 0.04 and 0.05M, the reverse was also true. These trends suggests that the retarding ability of the two inhibitors depends on the concentration of H_2SO_4. Correlation between E_a values for norfloxacin and sparfloxacin at different concentrations were weak(r=0.2031, 0.2864, -0.68677 and 0.0503 for H_2SO_4 concentrations of 0.01, 0.02, 0.03, 0.04 and 0.05M respectively). Confirming that norfloxacin and sparfloxacin exhibit different retarding strength for the corrosion of zinc in 0.01 -0.05M H_2SO_4.

Values of degree of surface coverage calculated for orfloxacin and sparfloxacin from equation 2 were used to fit curves for different adsorption isotherms including lagmuir, Freundlich, Florry Huggins, Frumkin and Temkin isotherms. Lagmuir adsorption isotherm was best applicable for the adsorption of norfloxacin and sparfloxacin on zinc electrode. According to Lagmuir isotherm, the surface coverage(θ) is related to te concentration of the inhibitor in the bulk solution by equation 7[16-20]:

$$\theta = kC(1 + kC) \quad\quad (8)$$

where k is the equilibrium constant for the adsorption process. Rearrangement of equation 8 gives equation 9:

$$C/\theta = 1/k + C \quad\quad (9)$$

By plotting C/θ versus C for norfloxacin and sparfloxacin at 303-323K, straight lines (Figure 10 and 11) were obtained (with R^2 values ranging from 0.8897-1.000 for norfloxacin and from 0.8767-1.000 for sparfloxacin) indicating that norfloxacin and sparfloxacin are adsorbed on zinc electrode according to the Lagmuir adsorption isotherm. In both cases, lines on the respective isotherms were very close to each other indicating that the mechanism of adsorption of different concentrations of norfloxacin and sprafloxacin are similar. Intercepts of lines on Lagmuir plot leads to values of equilibrium constant (k).

The equilibrium constant, k for the adsorption of norfloxacin is related to free energy of adsorption (ΔG_{ads}) according to equation 10[13-15]:
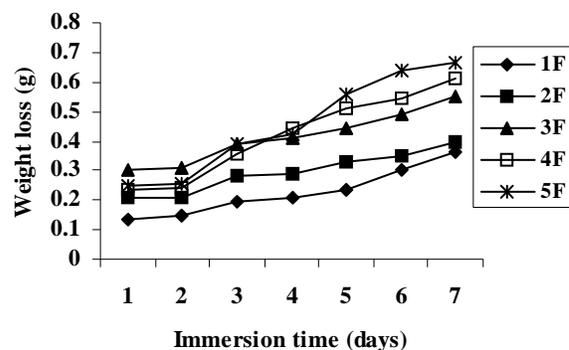
Figure 3a: A plot of weight loss versus immersion time for the corrosion of zinc in 0.05M(F) acid in the presence of 0.0001-0.0005M (1-5) norfloxacin at 303K
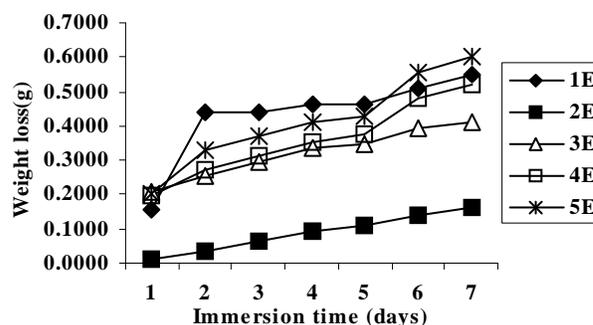
Figure 3: A plot of weight loss versus immersion time for the corrosion of zin in 0.05M(D) acid in the presence of 0.0001-0.0005M(1-5) of sparfloxacin at 303k

$$\Delta G_{ads} = -2.303RTlog(55.5k) \quad\quad (10)$$

Values of the free energy of adsorption (TABLE 1) of norfloxacin and sparfloxacin on zinc electrode (immersed in 0.01-0.03M) were nearer to 40KJ/mol (in most cases) indicating that inhibition of zinc corrosion by norfloxacin and sprafloxacin is govern by chemical adsorption[2]. The negative values of ΔG_{ads} indicates spontaneous adsorption of norfloxacin and sprafloxacin on the zinc surface[6-7]. For norfloxacin, at H_2SO_4 concentration of 0.01-0.03M, the inhibition process is much favoured as the temperature increases indicating that chemical adsorption of norfloxacin on zinc electrode dominate. But for sparfloxacin, the reverse was the case except at H_2SO_4 concentrations of 0.04 and 0.05M. A significant difference between values of free energy of adsorption for both inhibitors was observed (P≥0.05). Also, correlation between them was weak (r= 2.8017) indicating that the magnitude of adsorption behaviour of sparfloxacin significantly differ from that of norfloxacin.

The enthalpy of adsorption can be calculated from
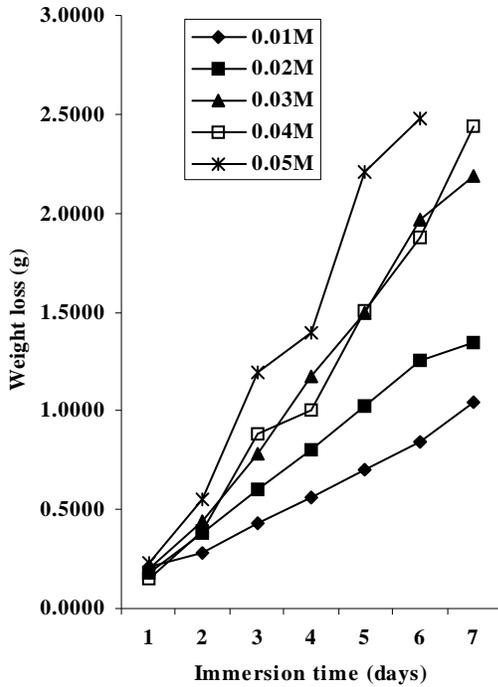
Figure 4: A plot of weight loss versus immersion time for the corrosion of zinc in 0.01-0.05M tetraoxosulphate (VI) acid at 303K

Figure 5a: Arrhenius plot for the corrosion of zinc in 0.01M acid in the presence of norfloxacin

Figure 5: Arrhenius plot for the corrosion of zinc in 0.01M acid in the presence of sparfloxacin

the Gibb-Helmholtz equation (6):
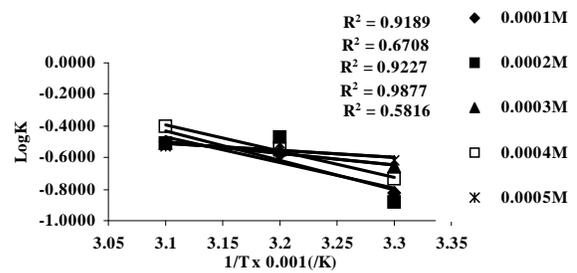
Figure 6a: Arrhenius plot for the corrosion of zinc in 0.02M acid in the presence of norfloxacin
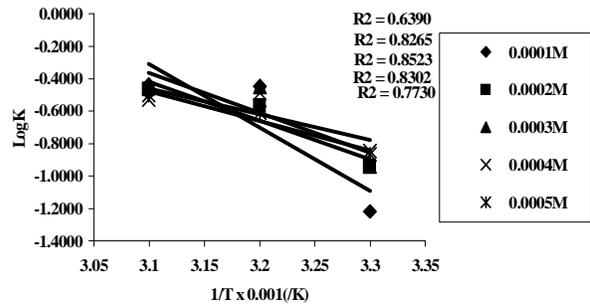
Figure 6: Arrhenius plot for the corrosion of zinc in 0.02M acid in the presence of sparfloxacin
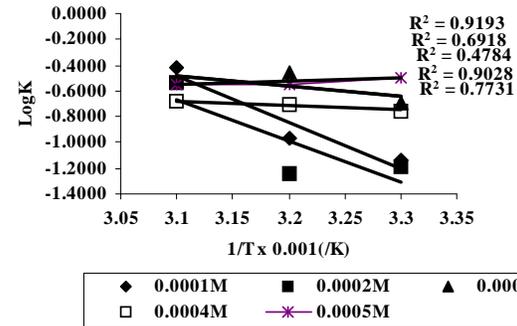
Figure 7a: Arrhenius plot for the corrosion of zinc in 0.03 M acid in the presence of norfloxacin
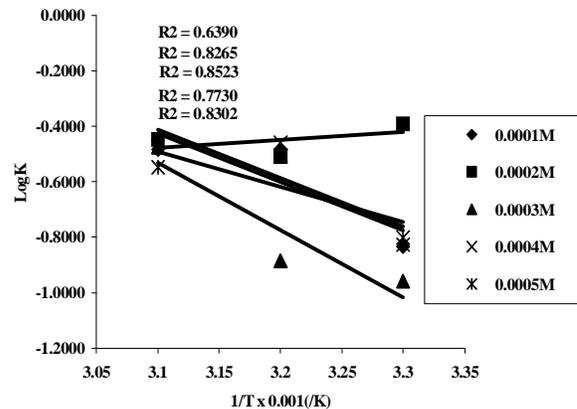
Figure 7: Arrhenius plot for the corrosion of zinc in 0.03M acid in the presence of sparfloxacin

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R2 = 0.5041
R^2 = 0.8338
R^2 = 0.9892
R^2 = 0.7274
R^2 = 0.6844

◆ 0.0001M
■ 0.0002M
▲ 0.0003M
□ 0.0004M
✳ 0.0005M

Figure 8a: Arrhenius plot for the corrosion of zinc in 0.04 M acid in the presence of norfloxacin

R2 = 0.6390
R2 = 0.8265
R2 = 0.8523
R2 = 0.7730
R2 = 0.8302

◆ 0.0001M   ■ 0.0002M   ▲ 0.0003M
✕ 0.0004M   ✳ 0.0005M
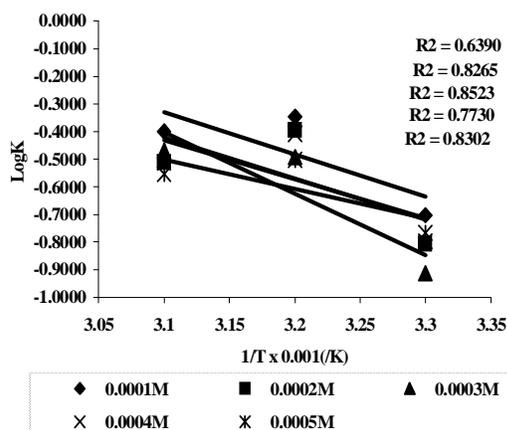
Figure 8: Arrhenius plot for the corrosion of zinc in 0.04M acid in the presence of sparfloxacin

$$[\delta(\Delta G_{ads}/T)]/\delta T=\Delta H_{ads}/T^2 \qquad (11)$$

Rearranging and integrating equation 11, equation 12 is obtained:

$$\Delta G_{ads}/T=\Delta H_{ads}/T \qquad (12)$$

From equation 12, a plot of $\Delta G_{ads}/T$ versus $1/T$ should give a straight line with slope equal to ΔH_{ads}(Figure 12and 13). Values of ΔH_{ads} are all negatives(TABLE 1) indicating that adsorption of norfloxacin and sparfloxacin on zinc electrode is exothermic. The magnitude of ΔH_{ads} is less negative for adsorption at H_2SO_4 concentrations of 0.04 and 0.05M (for norfloxacin) compares to adsorption at 0.01-0.05M. This indicates that norfloxacin is adsorbed more strongly at H_2SO_4 concentration of 0.01-0.03M sparfloxacin is more adsorbed at H_2SO_4 concentration range of 0.04 and 0.05M. The strength of the adsorption can further be attributed to the formation of strong electrostatic bond(at H_2SO_4 concentration of 0.01-0.03M) compares to weak bond when the concentration of H_2SO_4 is increased from 0.04-0.05M for

R2 = 0.5041
R^2 = 0.7398
R^2 = 0.6548
R^2 = 0.7391
R2 = 0.5061

◆ 0.0001M   ■ 0.0002M   ▲ 0.0003M
□ 0.0004M   ✳ 0.0005M
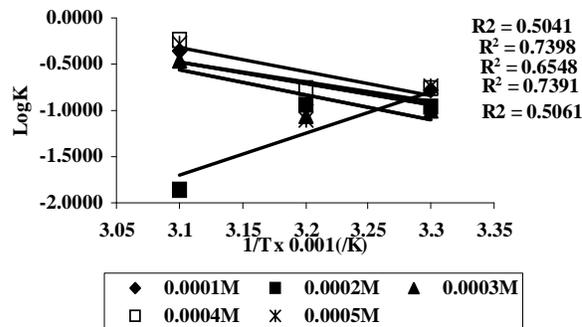
Figure 9a: Arrhenius plot for the corrosion of zinc in 0.05M acid in the presence of norfloxacin

R2 = 0.6390
R2 = 0.8265
R2 = 0.8523
R2 = 0.7730
R2 = 0.8302

◆ 0.0001M   ■ 0.0002M   ▲ 0.0003M
✕ 0.0004M   ✳ 0.0005M
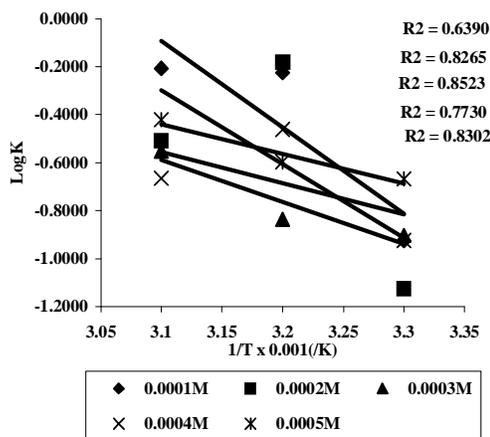
Figure 9: Arrhenius plot for the corrosion of zinc in 0.05M acid in the presence of sparfloxacin

◆ 303K(0.01)   ■ 313K(0.01)   △ 323K(0.01)   ✕ 303K(0.02)
✳ 313K(0.02)   □ 323K(0.02)   — 303K(0.03)   - 313K(0.03)
+ 323K(0.03)   ◇ 303K(0.04)   ■ 313K(0.04)   ▲ 323K(0.04)
⊠ 303K(0.05)   ⊠ 313K(0.05)   ○ 323K(0.05)
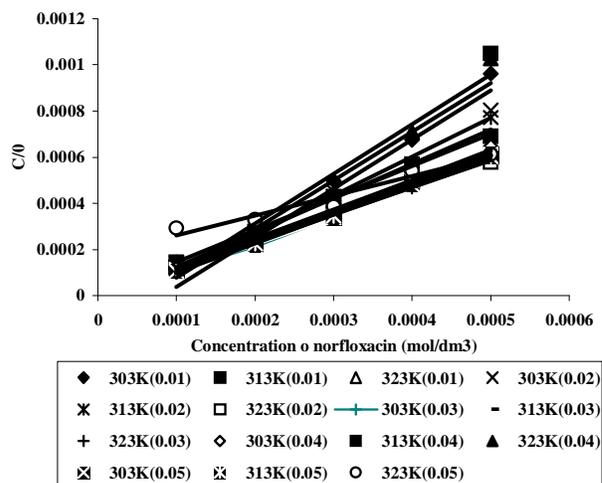
Figure 10: Curve fitting for adsorption of norfloxacin on zinc surface according to Lagmuir isotherm

norfloxacin and vice versa. It is also proposed by the authors that as the concentration of H_2SO_4 increases above 0.03M, influences of acidity on solvation and adsorption of norfloxacin competes with other factors
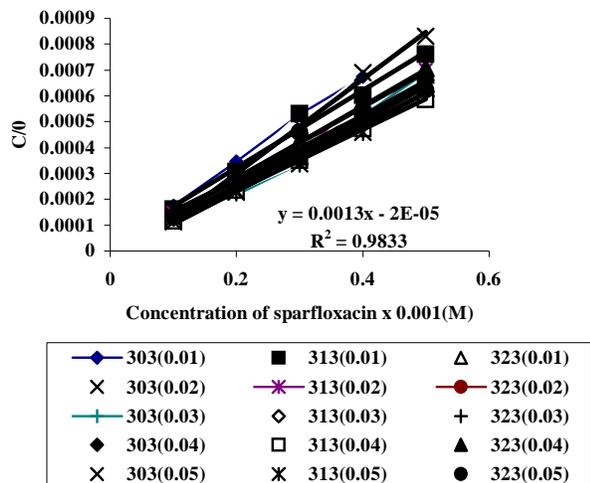
Figure 11: Curve fitting for adsorption of sparfloxacin on zinc electrode according to Lagm
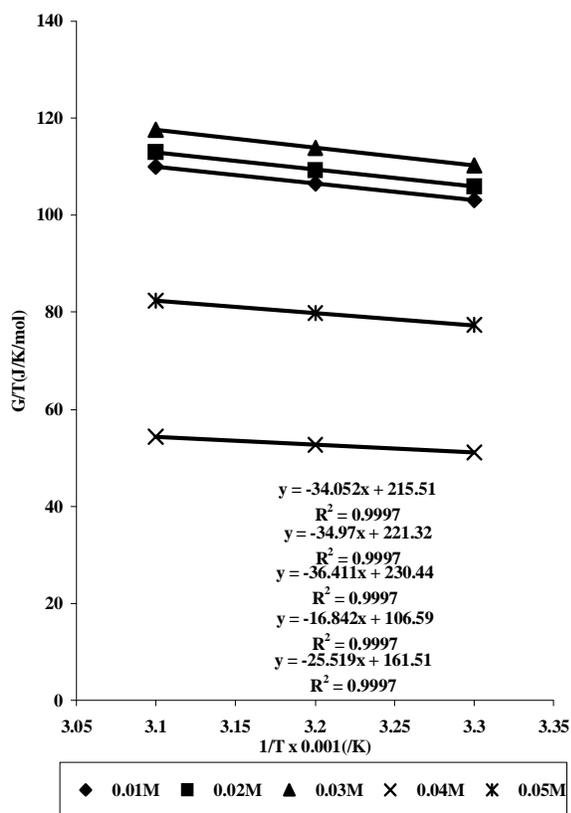
Figure 12: Variation of G/T with 1/T for norfloxacin

to weaken or strengthen the adsorption bond. Values of enthalpy of adsorption for norfloxacin significantly differ from values obtained for sparfloxacin ($P \geq 0.05$) and correlation between them was also weak ($r = 0.4786$).

Inhibition efficiency and mechanism of inhibition by sparfloxacin and norfloxacin

TABLE 2: Inhibition efficiency of 0.0001-0.0005M sparflo xacin in 0.01M-0.05M H_2SO_4

Con (mol/dm³)	0.01M tetraoxosulphate (VI) acid			0.02M tetraoxosulphate (VI) acid		
	303K	313K	323K	303K	313K	323K
0.0001	57.07	62.22	72.89	80.6	68.21	82.7
0.0002	57.66	64.97	69.8	70.54	72.64	83.06
0.0003	56.8	56.57	70.17	61.99	70.71	84.51
0.0004	59.27	66.42	70.09	57.89	77.44	84.51
0.0005	34.64	65.71	73.5	60.24	71.21	84.48

Con (mol/dm³)	0.03M tetraoxosulphate (VI) acid			0.04M tetraoxosulphate (VI) acid		
	303K	313K	323K	303K	313K	323K
0.0001	74.76	76.71	84.61	82.63	86.79	67.95
0.0002	92.55	76.11	84.15	76.26	85.2	68.1
0.0003	89.15	66.67	81.4	81.29	85.72	82.47
0.0004	76.31	75.82	81.47	75.64	84.67	68.76
0.0005	72.58	83.67	80.74	75.57	85.19	70.51

Con (mol/dm³)	0.05M tetraoxosulphate (VI) acid		
	303K	313K	323K
0.0001	88.1	79.03	76.63
0.0002	85.87	87.26	78.32
0.0003	82.01	89.18	65.47
0.0004	77.88	87.12	76.81
0.0005	79.19	77.54	80.23

TABLE 3: Inhibition efficiency of 0.0001-0.0005M norfloxacin in 0.01M-0.05M H_2SO_4

Con (mol/dm³)	0.01M tetraoxosulphate (VI) acid			0.02M tetraoxosulphate (VI) acid		
	303K	313K	323K	303K	313K	323K
0.0001	78.39	70.19	85.01	82.84	70.88	81.33
0.0002	85.59	72.40	82.73	84.56	75.16	87.73
0.0003	60.38	70.19	79.96	66.55	70.02	87.06
0.0004	59.18	70.19	79.58	72.55	80.30	82.48
0.0005	51.98	72.40	80.35	62.26	64.88	86.54

Con (mol/dm³)	0.03M tetraoxosulphate (VI) acid			0.04M tetraoxosulphate (VI) acid		
	303K	313K	323K	303K	313K	323K
0.0001	92.46	86.69	82.06	80.36	81.23	69.92
0.0002	94.47	92.87	83.07	89.09	82.11	62.19
0.0003	87.93	81.93	78.24	87.34	79.49	67.89
0.0004	81.40	85.26	84.92	80.36	76.43	56.27
0.0005	79.89	85.74	81.36	77.31	47.63	48.66

Con (mol/dm³)	0.05M tetraoxosulphate (VI) acid		
	303K	313K	323K
0.0001	89.93	95.20	34.30
0.0002	91.71	89.09	61.04
0.0003	89.09	86.91	77.83
0.0004	83.42	79.92	74.02
0.0005	81.67	82.98	81.64

TABLE 2 and 3 shows inhibition efficiency of sparfloxacin and norfloxacin. Inhibition efficiencies of sparfloxacin and norfloxacin are influenced by temperature, concentration of sparfloxacin/norfloxacin and concentration of acid. On the average, inhibition efficiency

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y = -88.685x + 399
R^2 = 0.8546
y = -70.255x + 348.28
R^2 = 0.7717
y = -17.659x + 174.81
R^2 = 0.4763
y = -24.578x + 213.61
R2 = 0.6236
y = 38.195x - 2.7143
R^2 = 0.9997

◆ 0.01M
■ 0.02M
▲ 0.03M
✕ 0.04M
✳ 0.05M
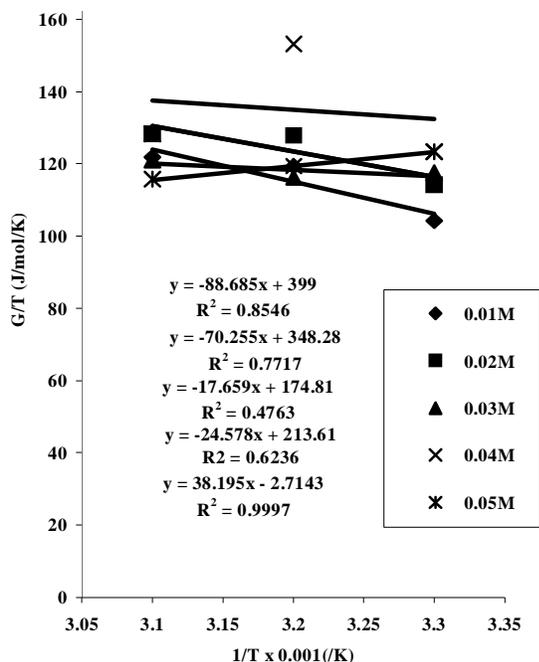
Figure 13: Variation of G/T with 1/T for sparfloxacin
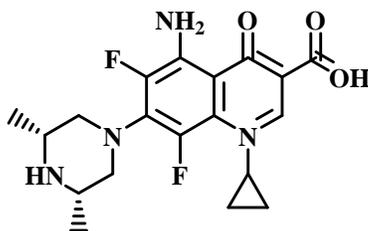
Figure 14: Chemical structure of sprafloxacin
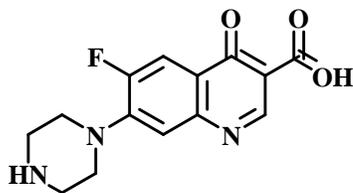
Figure 15: Chemical structure of norfloxacin

of both inhibitors increases as the concentrations of H_2SO_4 increases. Enhancement of inhibition efficiency of the studied compounds by increased concentration of tetraoxosulphate(VI) implies that adsorption of the used inhibitors is more activated at higher concentration of acid than at lower concentrations.

The molecular mass of sprafloxacin and norfloxacin are 392.41g/mol and 319.33g/mol respectively. A careful inspection of TABLE 2 and 3 reveals that inhibition efficiency of sparfloxacin at different temperatures and concentrations are relatively higher than corresponding

efficiencies obtained for norfloxacin. Several reasons may be responsible for the observed trend. First, inhibition efficiency of most inhibitor increases as the molar mass of the inhibitor increases[17-20]. Secondly, the present of amino group and extra fluorine atom in sparfloxacin which are absent in norfloxacin might have enhanced electron donating effect of sparfloxacin compare with norfloxacin, which has just one fluorine atom.

From the above, the following mechanism is proposed for the inhibition of zinc corrosion by sparfloxacin and norfloxacin;

i. In acidic medium, the inhibitors undergo dehydration to yield anhydronorfloxacin and anhydrospar floxacin which suffers further cleavages and lactorization .

ii. Dilute acid promotes epimerization of carbon atoms therefore, it is propose that adsorption of the inhibitors on zinc surface is stabilized by each molecule of the inhibitor donating electron to a vacant orbital of zinc.

The proposed mechanism is supported by relatively high values of activation energy, moderate values of enthalpy changes and negative values of entropy change which indicates the formation of a stabilised complex.

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