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Effect of 7-fluoro (a) and 5-amino/floro (b) substituents on inhibition efficiency of quinoline carboxylic acid for the corrosion of zinc in 0.01m H_2SO_4 medium

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ABSTRACT

Effect of 7-Flouro and %-amino groups on inhibition of the corrosion of zinc by quinoline carboxylic acid has been studied. Both compounds are found to inhibit the corrosion of zinc in 0.01M H_2SO_4. Inhibition efficiency of the two compounds is found to increase with temperature and decreases with concentrations. Values of thermodynamics parameters calculated for both inhibitors were comparable. However, values of inhibition efficiency of flouro substituted carboxylic acid were higher than values obtained for amino/flouro substituted carboxylic acid.

KEYWORDS

Zn corrosion;
Inhibition;
Quinoline carboxylic acid.

INTRODUCTION

Corrosion is an environmental problem resulting from contact of a metal or its alloy acidic or basic medium[1-7]. Temperature and corrodent;s concentration are the major factors responsible for the corrosion of metals[7-10] In most cases, the rate of corrosion of metals increases as the temperature and corrodent's concentration increases[8-12]. The environmental implication is that corrosion of metals is prevalent in industrial areas where acid rain and global warming are common.

The use of inhibitors has been found to be one of the best methods of fighting against corrosion of metals[10-12]. Most inhibitors are either synthesised from cheap raw materials or are chosen from organic compounds having electron rich bond and/or heteroatoms in long carbon/aromatic chain[7-15]. In practice choosing and confirming the inhibitive action of any compound requires thermodynamic, kinetic and adsorption considerations implying that models must be fashioned to present theoretical suitability of an inhibitor meant for field utilization. The present study is aimed at investigating effect of A and B on inhibition of the corrosion of zinc. The chemical structures of the compounds are shown by figure 1. From the structure, it is most probable that the compounds are good corrosion inhibitors.

MATERIALS AND METHODS

1. Materials

The sample (D) was synthesized by green chemistry method[7]. Zinc specimens used for the study were of dimension of 5×4×0.11cm. The acid solutions (H_2SO_4) were prepared from analar grade manufac-

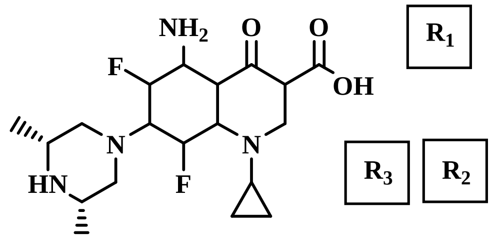

Figure 1: chemical structure of A and B, For A, R_1= H, R_2= CH_3, R_3= H. For B, R_1=NH_2, R_2=CH_3 and R_3= F;

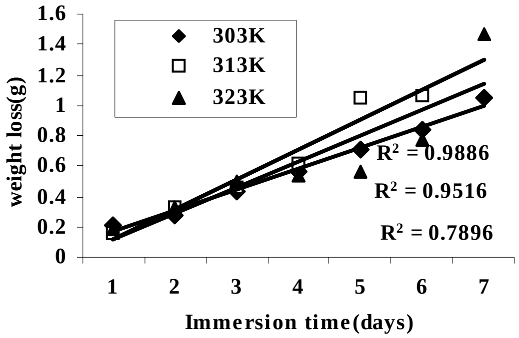

Figure 2b: Weight loss of zinc versus immersion time (blank)

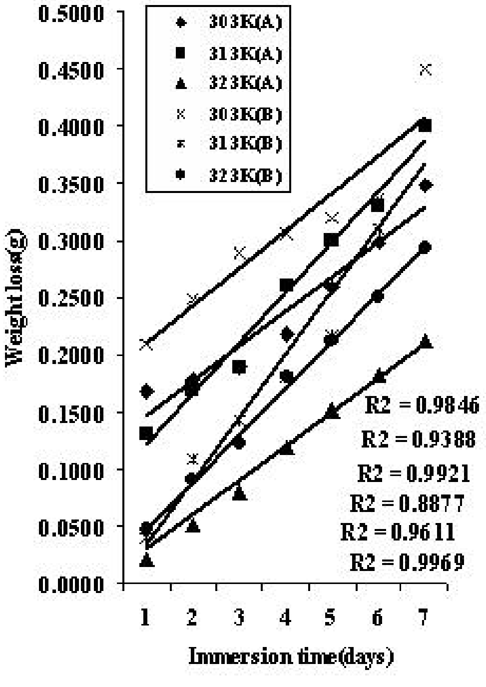

Figure 2: Weight loss for the corrosion of zinc in the presence of 0.00001MA and 0.00001MB at 303-323K

tured by BDH chemicals. Each mild steel coupon was washed in ethanol, dried by dipping in acetone and preserved in a dessicator prior to their used..

2. Weight loss measurement

Weight loss measurements were carried out as described in literature[9-10]. Each specimens of the mild steel coupon was immersed in separate beakers containing 250ml of 0.0001-0.0005M of A(each dissolved in 0.01M H_2SO_4) and to another beaker containing 250ml of 0.01M H_2SO_4 to serve as the control (blank). Each set of experiments were carried out at different thermostated conditions (303, 313 and 323K) after every 24hours period of immersion for a total period of 168hours. Prior to weight loss measurement, each coupons were 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 with scaltec high precision balance (Model SPB31) having 4 decimal place sensitivity.

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

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

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

$$CR=534W/pAt \qquad (3)$$

where W_1 and W_2 are the weight losses (in g) for mild steel in the presence and absence of A/B. W = $W_{2-}W_1$., p is the density of the mild steel specimen in g/dm³, A is the area of the specimen in square inch and t is immersion time in hours.

Gasometric method

Gasometric methods were carried out as described in literature[2-4]. From the volume of hydrogen evolved per minutes, inhibition efficiency of the used inhibitor was calculated using equation 4

$$I(\%) = \{1 - \frac{V'_{Ht}}{V^0_{Ht}}\} \times 100 \qquad (4)$$

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

1. Effect of concentration and temperature on weight loss of zinc

Figures 2-4 show plots of weight loss of zinc in 0.01M H_2SO_4 in the presence of different concentrations of A and B respectively (inserted are plots of weight loss versus time for different concentrations of H_2SO_4). From the plots, three major trends can be observed.

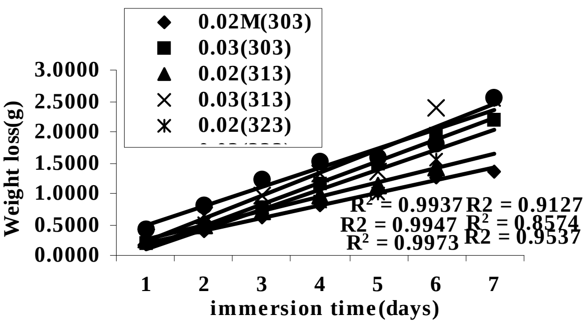

Figure 3a: Weight loss of zinc in 0.02 and 0.03M

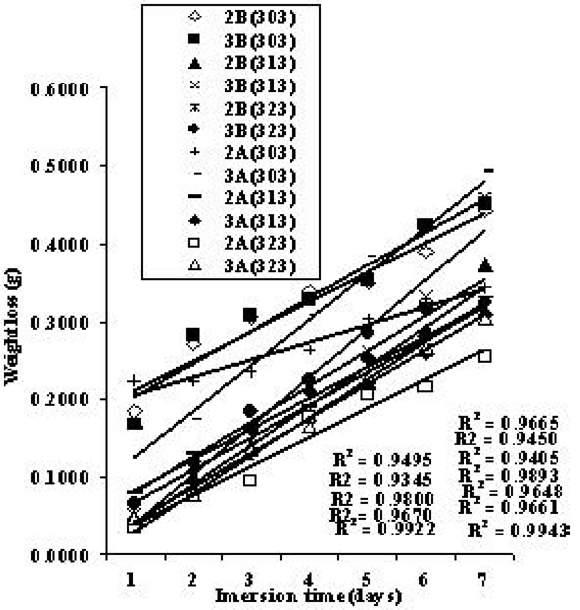

Figure 3: Weight loss of zinc in the presence of 0.0002(2A/B) and 0.0003(3A/B) of A and B at different temperature (303-323K)

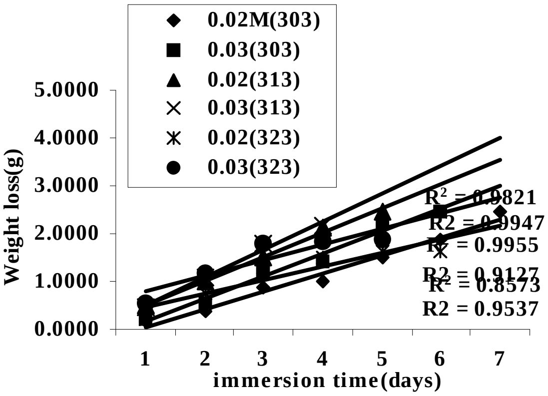

Figure 4a: Weight loss of zinc in 0.04 and 0.05M

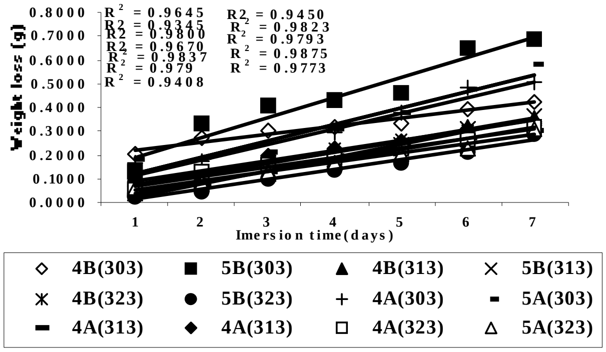

Figure 4: Weight loss of zinc in the presence of 0.0004(4A/B) and 0.0005(5A/B) of A and B at different temperature (303-323K

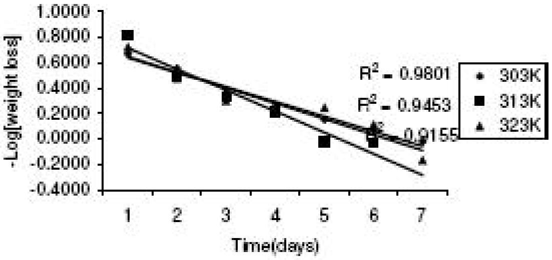

Figure 4b : Kinetic plot for the corrosion of zinc(blank)

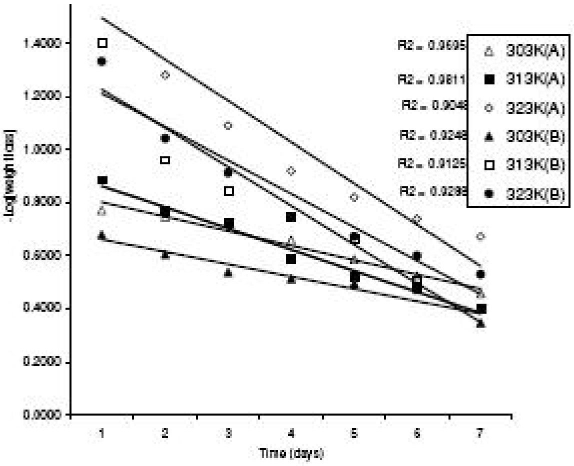

Figure 4: Kinetic plot for the corrosion of zinc in the presence of 0.0001MA and 0.0001M B

First, at constant temperature, average weight loss of zinc electrode in 0.01M H_2SO_4 in the presence of 0.0001-0.0005M A and B were found to increase with concentration of A or B. Secondly, at constant concentration, average values of weight losses of zinc electrodes were found to increase with temperature except at concentrations of 0.0001M A, 0.0002MB and 0.0003M B were three were slight increase in weight loss before the decrease at 323K. Lastly, the corrosion of zinc in H_2SO_4 tend to increase as the concentration of H_2SO_4 and is temperature increased.

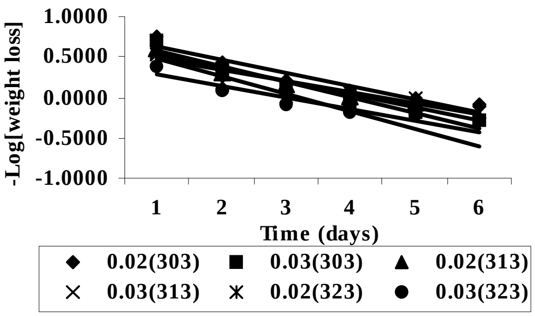

Figure 5b: Kinetic plot for corrosion of zinc in 0.04 and 0.05M tetraoxosulphate (VI) acid

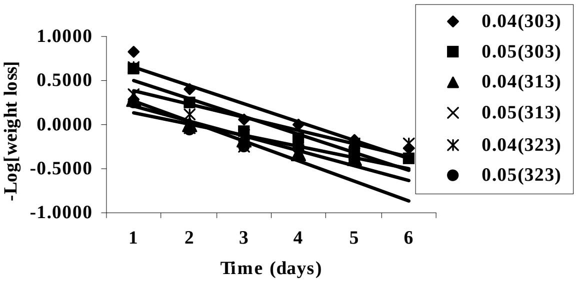

Figure 6b: Kinetic plot for corrosion of zinc in 0.04 and 0.05M tetraoxosulphate (VI) acid

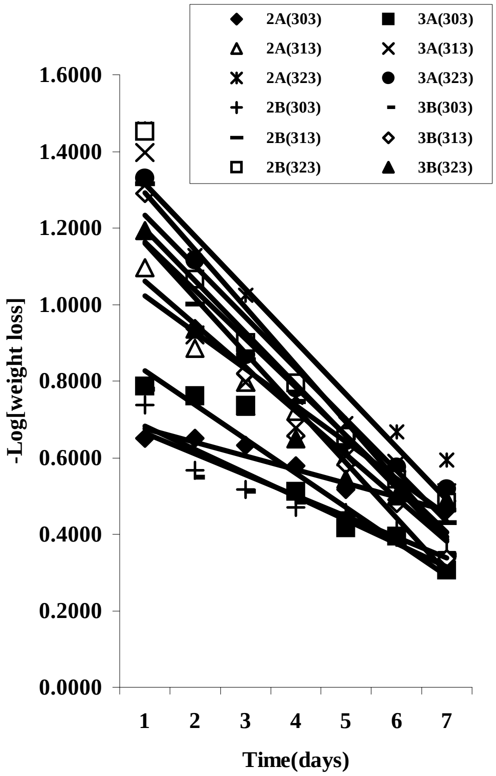

Figure 5: Kinetic plot for the corrosion of zinc in the presence of 0.0002(2A/B)-0.0003M(3A/B) of A and

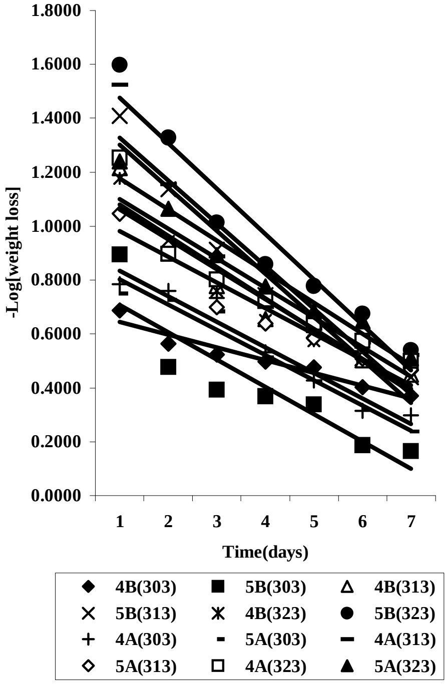

Figure 6: Kinetic plot for the corrosion of zinc in the presence of 0.0004(4A/B)-0.0005M(5A/B) of A and B

2. Kinetics, adsorption and thermodynamics considerations

The dissolution reaction of zinc in H_2SO_4 can be represented by equation 5:

$$Zn(s)+H^+ \longrightarrow Zn^{2+}+H_2 \qquad (5)$$

From equation 5, the rate of dissolution of zinc can be written as follows,

$$\frac{d[Zn_{(s)}]}{dt} = K_1[Zn_{(s)}]_0 \qquad (6)$$

where$[Zn_{(s)}]$ and$[Zn_{(s)}]_o$ are the concentrations of zinc at time, t=0 and at time t. Following the initial conditions,$[Zn_{(s)}]=[Zn_{(s)}]_o$ at t=0 and assuming that the corrosion reaction is controlled by the forward reaction, then equation 6 can be transformed to equation 7[2-4]:

$$[Zn_{(s)}]=[Zn_{(s)}]_o exp(-kt) \qquad (7)$$

where K_1 is the rate constant of the corrosion reaction of zinc Integrating equation 7, equation 8 is obtained:

$$ln[Zn_{(s)}]-[Zn_{(s)}]_o=-K_1t \qquad (8)$$

If assumptions establishing equation 8 are valid, then a plot of -log[weight loss] of zinc versus time should produce a straight with slope equal to $K_1/2.303$. Plotting of values of weight loss of zinc with respect to different concentrations of H_2SO_4 and A (0.0001M-0.0005M)/B(0.0001-0.0005M) yielded straight lines

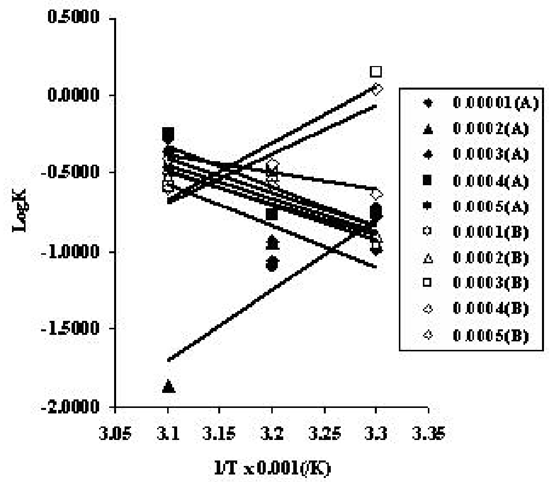

Figure 7:Arrhenius plot for the corrosion of zinc in the presence of 0.0001-0.0005M A and B

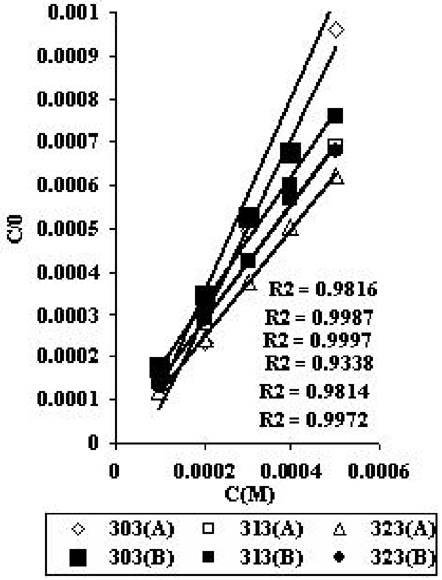

Figure 8: Curve fitting for adsorption of A and B on zinc surface according to Lagmuir adsorption isotherm

(Figures 4-6) implying that the corrosion reaction of zinc in the presence and absence of A and B proceeded according to first order kinetics. Values of rate constants at various temperatures and temperatures were obtained from slopes of lines on the plots.

Values of K_1 obtained from kinetics plots were used to calculate the activation energy of the corrosion reaction of zinc according to Arrhenius equation(9):

$$K=A\exp(-E_a/RT) \quad (9)$$

where E_a is the activation energy of the corrosion reaction of zinc, R is the gas constant and A is Arrhenius or pre-exponential constant. Taking logarithm of both sides of equation 9, equation 10 is obtained[12-17]:

TABLE 1:Thermodynamic parameters of adsorption of A and B on zinc electrode

Concentration of inhibitor (mol/dm^3)	(E_a)J/mol	
	A	B
0.0001	39.7264	41.30804
0.0002	-86.8074	42.1352
0.0003	51.5460	-70.2336
0.0004	49.6562	-60.3882
0.0005	43.2897	21.25333
ΔS_{ads} (J/mol)	303.35	303.35
ΔH_{ads} (KJ/mol)	-68.369	-67.0177
Temperature (K)	ΔG_{ads} (KJ/mol)	
303	-23.2063	-23.2063
313	-31.3166	-27.2615
323	-29.2734	-29.274

$$\log K=\log A-E_a/2.303RT \quad (10)$$

From equation 9, plotting of logK versus 1/T should give a straight line with slope equal to $-E_a/2.303R$ and intercept equals to logA. Values of logK plotted against 1/T (Figure 7) yielded straight lines (R^2 ranged from 0.08867-0.9876) for both inhibited and uninhibited corrosion reactions of zinc. From slopes of lines on each plot, respective values of E_a were calculated. Values of E_a (TABLE 1) for uninhibited corrosion reaction of zinc were negative and lower than values obtained for reactions inhibited by either A or B. This indicate that A and B retards the corrosion reaction of zinc in 0.01M H_2SO_4.. However, although values of E_a obtained for A were relatively comparable to values obtained for B, correlation between them was weak (R^2 = 0.2955).

Adsorption isotherms are very important in understanding the mechanism of inhibition of corrosion reaction of zinc. The most frequently used adsorption isotherms are Frumkin, Temkin, Freundlich, Florry Huggins, Bockris-Swinkel, El-Awardy and Lagmuir isotherms. All these isotherms can be represented as follows,

$$f(\theta, x)\exp(-2a\theta)=kC \quad (11)$$

where $f(\theta, x)$ is the configuration factor which depends upon the physical model and the assumptions underlying the derivation of the isotherm. θ is the degree of surface coverage, C is the inhibitor concentration in the electrolyte, X is the size ration, a is molecular interaction parameter and k is the equilibrium constant of the adsorption process. Adsorption of A and B on zinc electrode were better explained by Lagmuir isotherm. According to assumptions of Lagmuir, the concentration of the adsorpbate (A/B) in the bulk of the electrolyte (C) is related to degree of surface coverage (θ) by equation 12[15-20]:

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

Figure 6 and 7 show Lagmuir plots for adsorption of A and B on zinc surface respectively. The fact that plots of C/θ were linear (R^2 ranged from 0.8765-1.000) implies that Lagmuir adsorption isotherm is applicable for the adsorption of A and B on zinc electrode and that the adsorption of A and B on zinc electrode is[6-9].

From intercepts of respective lines on the Lagmuir adsorption plot (Figure 8), values of equilibrium constant of adsorption (k) were obtained. The equilibrium constant of adsorption is related to free energy of adsorption (ΔG_{ads}) according to equation 13

$$\Delta G_{ads} = -RT\ln(55.5k) \qquad (13)$$

Values of ΔG_{ads} calculated from equation 13 were negatives and close to threshold values required for chemical adsorption (TABLE 1) implying that adsorption chemical adsorption mechanism is applicable to adsorption of A and B on zinc electrode

Thermodynamic parameters of adsorption (ΔH_{ads} and ΔS_{ads}) were computed by using Gibb Helmholtz equation:

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \qquad (14)$$

From equation 14, plotting of ΔG_{ads} versus T should give a straight line with slope equal to ΔS_{ads} and intercept equal to ΔH_{ads}. Values of ΔH_{ads} and ΔS_{ads} are recorded in Table 1.From the results, it can be seen that the adsorption of A and B is exothermic.

3. Inhibition efficiency of A and B

TABLE 2: Values of inhibition efficiency of A and B at different temperatures

Con (mol/dm^3)	A			B		
	303K	313K	323K	303K	313K	323K
0.0001	78.39	70.19	85.01	57.07	62.22	72.89
0.0002	85.59	72.40	82.73	57.66	64.97	69.8
0.0003	60.38	70.19	79.96	56.8	56.57	70.17
0.0004	59.18	70.19	79.58	59.27	66.42	70.09
0.0005	51.98	72.40	80.35	34.64	65.71	73.5

Con. (mol/dm^3)	Thermometric method	
	A	B
0.0001	87.43	67.54
0.0002	90.44	63.76
0.0003	69.89	62.66
0.0004	64.35	70.46
0.0005	60.32	50.12

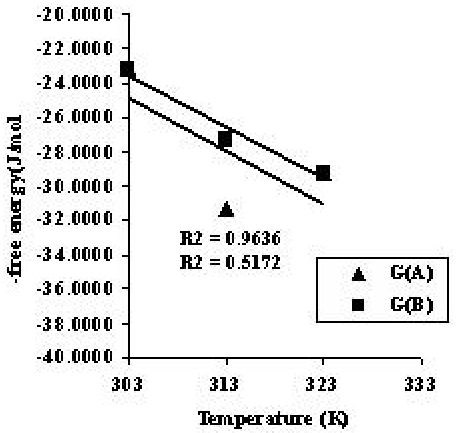

Figure 9: Effect of temperature on the standard free energy of adsorption of A and B on zinc surface

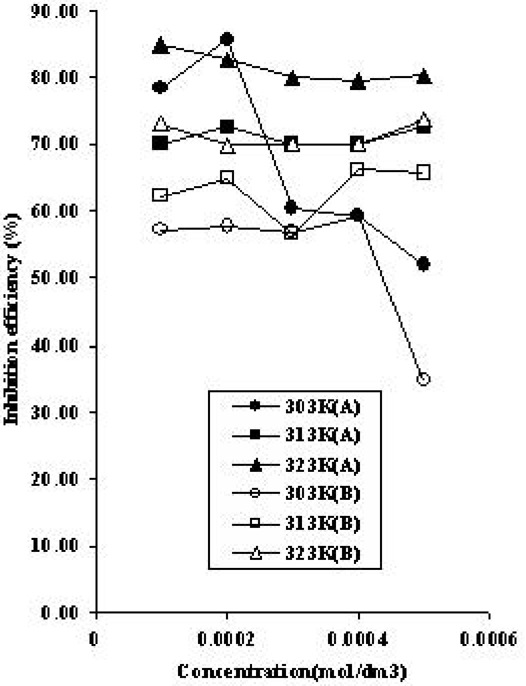

Figure 10: Variation of inhibition efficiency of A and B with concentration at different temperatures

Values of inhibition efficiency of A and B calculated from equation 1 are recorded in TABLE 2. It is seen that values of inhibition efficiency of A are higher than those of B at similar temperature and concentration. From the chemical structures of A and B , it can be seen that the two compounds have similar parent structure but B has additional flourine and amino group compare to A which has only one fluorine. In addition, the molecular mass of B is greater than that of A. As a rule, the inhibition efficiency of B is expected to be greater than that of B but this was not observed in this study.. It

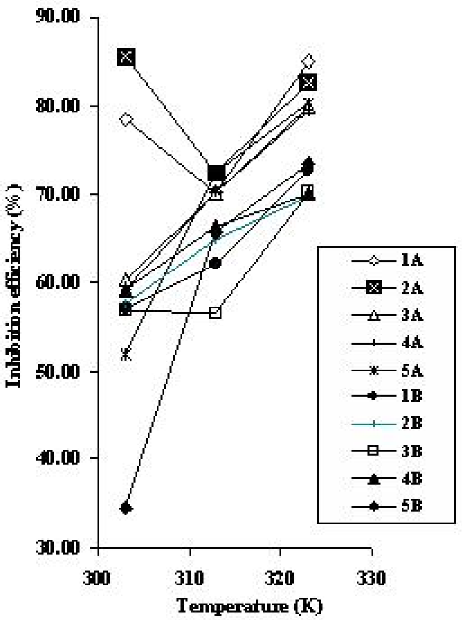

Figure 11: Variation of inhibition efficiency of A and B with temperature(1A, 1B = 0.0001MA & 0.0001MB, etc]

is believe that the presence of amino group in B hindered the ease of donation of electron for the formation of zinc-inhibitor complex. Thus decreasing its inhibition efficiency.

Variation of inhibition efficiency with concentration is shown by figure 10 while figure 11 shows variation of inhibition efficiency of A and B with temperature. The figures reveals that inhibition efficiency of A and B increases as the temperature increases and decreases as the concentration of the inhibitor increases. The trend for the variation of inhibition efficiency of A and B with temperature was A(323K)>B(323K)>A(313K) >B(313K)>A(303K)>B(303K).

Values of inhibition efficiency of A and B obtained from gasometric method were relatively higher than values obtained from weight loss measurement. This is due to the fact that weight loss method measures average values of corrosion rate while gasometric method measures instantaneous values of corrosion rate. However, values obtained from weight loss at 303K correlated strongly with values obtained from gasometric method for both A(R^2=0.9765) and B(R^2=0.8871) implying that A and B are good corrosion inhibitors for zinc..

CONCLUSIONS

From the study, the following conclusions are made,

i. Both compounds inhibit the corrosion of zinc in 0.01M H_2SO_4 at 303-323K.

ii. Inhibition efficiency of both compounds increases with temperature and decreases with concentration.

iii. The inhibitors are adsorption inhibitors been spontaneously adsorbed on zinc electrode according to Lagmuir adsorption isotherm.

iv. Values of thermodynamics parameters and inhibition efficiency of A and B are comparable.

REFERENCES

[1] A.O.James, N.C.Oforka, K.Abiola; Intern.J. Electrochem.Sc., **2**, 284 **(2007)**.
[2] E.E.Ebenso, P.C.Okafor, U.J.Ekpe, U.J.Ibok, A.I. Onuchukwu; J.Chem.Soc.Nigeria **29**, 25 **(2004)**.
[3] E.E.Ebenso; Nigerian J.of Chem.Res., **6**, 12 **(2001)**.
[4] U.J.Ekpe, P.C.Okafor, E.E.Ebenso, O.E.Offiong, B.I.Ita; Bullentin of Electrochem., **17**, 135 **(2001)**.
[5] S.Muralidharan, R.Chandrasek, S.K.Iyer; Proc. Indian Acad.Sci., **112**, 136 **(2000)**.
[6] G.Tranbonella, V.Carassiti; Advances in corrosion sciences and Technology, Phenium press, New York,
[7] B.A.Mandell, T.A.Meredith, E.Aguilar, A.el-Massry, A.Sawant, S.Richard, P.L.Gutmann; J. Antimicrob.Chemother., **30**, 739-744 **(1992)**.
[8] K.S.Rayappa, T.V.Venkatesha; Turk.J.Chem., **27**, 196 **(2002)**.
[9] W.A.Monika, A.D.Siddique; Portugaliae Electro chimica acta, **23**, 455 **(2005)**; Sekine, Arzneimittel forschung, **41**, 746 **(1991)**.
[10] Emregul, R.Kurtaran, O.Atakol; Corrosion Sc., **45**, 2817 **(2003)**.
[11] O.K.Abiola; J.Childean Chem Soc., **4**, 690 **(2005)**.
[12] E.E.Oguzie; Pigment & resin Technology, **6**, 340 **(2006)**.
[13] E.E.Oguzie, E.E.Ebenso; Pigment & Resin Tech., **35**, 35 **(2006)**.
[14] P.Tavassoli-Salardini, Inhibition of corrosion of mild steel in aqueous solution.Ph.D Thesis, University of Sydney.
[15] M.Ehteshamzade, T.Shahrabi, M.G.Hosseini; Appl.Surf.Sc., **252**, 2959 **(2006)**.
[16] M.Abdallah; Corrosion Sc., **46**, 1996 **(2004)**.
[17] M.Abdallah; Corrosion Sc., **44**, 728 **(2002)**.
[18] K.Orubite-Okorosoye, N.C.Oforka; J.Appl.Sc and Environm.Mgt., **8**, 61 **(2004)**.
[19] S.D.Shetty, P Shetty and H.V.S.Nayak; J.Chilean Chem.Soc., **2**, 853 **(2006)**.
[20] P.W.Atkin; 'A textbook of physical chemistry', Oxford University press, 938 **(1991)**.