

INHIBITION OF CORROSION OF ZINC IN 0.01M H₂SO₄ BY 5-AMINO-1-CYCLOPROPYL-7-[(3*R*,5*S*)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 reactions of zinc is found to be first order. Values of rate constant and half-life ranged from 0.1076 – 1.10893 and from 24 – 154days respectively. An average value 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). Also average values of enthalpy change ($\Delta H_{ads} = -15.1751\text{J/mol}$) and entropy change ($\Delta S_{ads} = -279.8631\text{J/mol}$) indicated that the adsorption of A on zinc surface is exothermic and is accompanied by increase in degree of orderliness. Between 303 and 323K, values of free energy of adsorption (ΔG_{ads}) ranged from -84.7852 - -90.3805KJ/mol indicating that the adsorption of A is spontaneous and follows the mechanism of chemical adsorption. Lagmuir adsorption isotherm has been found to be applicable to the adsorption of A on mild steel surface.

Key Word: Zinc corrosion, inhibition, A

1. 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 its alloy [1-6.]. A search for a suitable inhibitor for the corrosion of zinc (in acidic medium) involves a choice between those synthesized 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 requires adequate attention. 5-amino-1-cyclopropyl-7-[(3R,5S)3,5-dimethylpiperazin-1-yl]-6,8-difluoro-4-oxo-quinoline-3-carboxylic acid (A) contained heteroatoms in their aromatic ring. It has a high molecular mass and can easily be synthesized by chemical method [7]. Due to its unique properties, A may be a good inhibitor for the inhibition of zinc corrosion. The present studies seek to investigate inhibitive properties of 5-amino-1-cyclopropyl-7-[(3R,5S)3,5-dimethylpiperazin-1-yl]-6,8-difluoro-4-oxo-quinoline-3-carboxylic acid (A) for the corrosion of zinc in 0.01M H₂SO₄.

2. Materials and methods

2.1 Materials

The sample (A) was by Livemore pharmacy, Ikot Ekpene, Nigeria. Zinc specimens used for the study were of dimension 5 x 4 x 0.11cm. The acid solutions (H₂SO₄) were prepared from analar grade manufactured by BDH chemicals. Concentration of acid used for weight loss experiment was 0.01M while 2.5M was used for gasometric experiment. Double distilled water was used for the preparation of all

reagents. The concentration range of inhibitor prepared for weight loss and gasometric studies was 0.0001 –0.0005M.

2.2 Weight loss measurement.

Weight loss measurements were carried out as described in literature [1-6]. The volume of solution used was 150ml. A maximum immersion time was 168hours. Solutions were not stirred but specimens were removed from their respective solutions after every 24hours, washed in 5% chromic acid solution containing 1% silver nitrate (in 10% aluminum chloride), rinsed in boiling water, dried in acetone and weighed. Weight loss experiments were carried out at different temperatures (303, 313, 323 and 333K) and different concentrations (0.0001 –0.0005M) of inhibitor were used.

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

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

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

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

2.3 Gasometric method

Gasometric methods were carried out as described in literature [11-13] Mild steel coupons of dimension similar to those used for weight loss method were also used for hydrogen evolution studied.

From the volume of hydrogen evolved after every minutes, inhibition efficiency of different concentration of A was calculated using equation 3

$$I(\%) = \left\{ 1 - \frac{V_{Ht}}{V_{Ht}^0} \right\} \times 100 \quad (3)$$

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 uninhibited solution

3.0 Results and discussion

3.1 Effect of concentration and temperature.

Fig. 1 shows weight loss of zinc (in 0.01M H_2SO_4) in the presence of 0.0001 – 0.0005M of A while Fig. 1b (inserted) shows weight loss of zinc (in 0.01M H_2SO_4) in the absence of the inhibitor. Comparing Fig. 1 with Fig. 1b, it can be seen that values obtained for weight losses of zinc in the presence of different concentration of A were generally lower than values obtained for the blank (Fig.1b) 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 temperatures and that the mechanism of adsorption of A on zinc electrode is chemical adsorption [14-15].

3.2 Kinetics and thermodynamics considerations

In order to study the kinetic of the inhibited corrosion reaction, attempts were made to fit data obtained from weight loss measurement into different kinetic plots including zero order, first and second order and by far the inhibited corrosion reaction was found to proceed via first order. For a first order reaction, the concentration of zinc $[Zn_0]$ at time $t = 0$ and the concentration after time t is related to each other according to equation 4 [16]:

$$-\log[Zn_0] - [Zn] = K_1 t / 2.303 \quad (4)$$

where K_1 is the rate constant for a first order reaction. By plotting values of $-\log[\text{weight loss}]$ versus time for the corrosion reactions of zinc in the presence and absence of A (Fig. 2 and 2a), straight lines were obtained implying that the corrosion reactions of zinc in the absence and presence of A proceeds according to first order kinetics.

Values of half life for the corrosion reaction of zinc in the absence and presence of A were calculated using equation 5[16]:

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

Calculated values of $t_{1/2}$ for inhibited corrosion reaction of zinc are recorded in Table 1. These values are found to be higher than values obtained for the blank indicating that A extends the half life of zinc corrosion.

In order to calculate the activation energy of the corrosion reaction of zinc in the absence and presence of A, the Arrhenius equation was used (equation 6) [16-17]:

$$K = \exp(-E_a/RT) \quad (6)$$

where K is rate constant obtained from the slope of kinetic plots (Fig. 2), E_a is the activation energy of corrosion reaction of zinc, R is the gas constant and T the is temperature. Transforming equation 6 to logarithm form, equation 7 is obtained:

$$\log K = -E_a/2.303RT \quad (7)$$

From equation 7, a plot of $\log K$ versus $1/T$ should produce a straight line with slope equals to $-E_a/2.303R$ from where the value of E_a can be computed. Fig. 4 shows Arrhenius plot for the corrosion of zinc in the presence of A. From the plot, calculated values of E_a ranged from 21.2552 – 70.2336J/mol(mean = 5.1751J/mol)(Table 2) implying that the E_a for inhibited corrosion reaction of zinc is higher than that of

uninhibited corrosion reaction of zinc (average $E_a = -13.0760 \text{ J/mol}$). The observed differences confirm that A retards the corrosion of zinc in H_2SO_4 .

In order to calculate thermodynamic parameters for the corrosion reaction of zinc, the transition state equation (equation 8) was used [16-17]:

$$K = \frac{RT}{Nh} \exp(\Delta S/R) \exp(-\Delta H/RT) \quad (8)$$

Rearranging equation 8, equation 9 is obtained.

$$\log(K/T) = \log R/Nh + \Delta S/2.303R - \Delta H/2.303RT \quad (9)$$

where N is the Avogadro's number and h is the plank constant. From equation 9, a plot of $\log K/T$ versus $1/T$ should produce a straight line with slope equals to $-\Delta H/2.303R$ and intercept equals to $\log R/Nh + \Delta S/2.303R$

Values of ΔH_{ads} (Table 2) calculated through slopes of lines on the transition state plot (Fig. 3) ranged from $-72.8913 - 39.4852 \text{ J/mol}$ (mean = -15.2737 J/mol) indicating that the inhibited corrosion reaction of zinc is exothermic. Also, values of ΔS_{ads} calculated from intercepts of lines on the plot (Fig.3) ranged from $-130.9684 - 484.4800 \text{ J/mol}$ (mean = -279.8631 J/mol) indicating 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 the Gibb-Helmoltz equation (equation 10) [16]:

$$\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\Delta S_{\text{ads}} \quad (10)$$

Calculated values of ΔG_{ads} are recorded in Table 2. the values ranged from $-84.7832 - -90.3805 \text{ J/mol}$ indicating that adsorption of A on zinc surface is spontaneous and proceeds via chemical adsorption mechanism. [10-15].

3.3 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.

Assumptions of Lagmuir adsorption isotherm relates concentration of inhibitor in the bulk electrolyte to the degree of surface coverage according to equation 11 [18-20]:

$$C/\theta = 1/K + C \quad (11)$$

where C is inhibitor's concentration, θ is the degree of surface coverage and K is the binding constant. From equation 11, if the assumptions of Lagmuir are obeyed, a plot of C/ θ versus C should give a straight line with intercept equals to 1/K [12] Lagmuir plot for the corrosion reaction of zinc in the presence of A is shown by Fig 4. The fact that lines on the Figures are linear and very close to each other confirms that Lagmuir adsorption isotherm is applicable to the adsorption of different concentration of A within the temperature range of 303 –323K. It also indicates that A causes a high increase in the free energy with respect to uninhibited system. These results show strong adsorption of inhibitors on the mild steel surface and suggest the existence of monolayers of adsorption [18-20].

From the intercept of Lagmuir plot (Fig. 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 the mechanism of chemical adsorption.

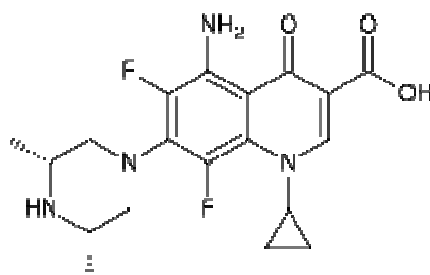
3.4 Inhibition efficiency of A

Values of inhibition efficiency of A calculated from weight loss measurement are recorded in Table 3. The result shows that Inhibition efficiency of A increase with temperature indicating that A is chemically adsorbed on zinc electrode. Fig. 6 shows a plot of variation of inhibition efficiency of A with concentration. Inserted (Fig.6a) is the plot showing the variation of inhibition efficiency of different concentration of A with temperature. From the Figure, it is obvious that inhibition efficiency of A vary slightly with concentration but largely with temperature.

The results obtained for inhibition efficiency of A from gasometric method compares favourably with results obtained from weight loss method at 303K ($r = 0.8288$) confirming that A inhibits the corrosion of zinc. .

3.5 Mechanism of inhibition

The used inhibitor 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 Structure I), the following inhibition mechanism is proposed for the used inhibitor (A):



Structure I

- i. In acidic medium, A undergoes dehydration to yield anhydrosparfloxacin which suffers further cleavages and lactonization
- ii. Dilute acid promotes epimerization of C-bonds, therefore, it is proposed that the 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 = 5.1751 J/mol) and other thermodynamic parameters. The fairly high negative values of entropy (mean = -279.8631 J/mol) of adsorption suggest the formation of a compact activated complex with fewer degrees of freedom.

4. Conclusion

From the results of the study, the following conclusions are drawn,

- i. A is a good inhibitor for zinc corrosion in H_2SO_4 . Inhibition efficiency of A is enhanced mainly by its structural properties.
- ii. Inhibited corrosion reaction of Zn is controlled by activation complex
- iii. Adsorption of A on zinc surface is spontaneous and proceeds via chemical adsorption mechanism.
- iv. Langmuir adsorption isotherm is best applicable to the adsorption of A on zinc electrode.

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6. References

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Table 1: Values of rate constant and half-life (days) for corrosion of Zn in 0.01M H₂SO₄ in the presence of 0.0001 – 0.0005M A

Con. mol/dm ³	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

Table 2: Thermodynamic parameters for the corrosion of zinc in 0.01 –0.01M H₂SO₄ in the presence of 0.0001 –0.0005M A

Con. mol/dm ³	E _a (J/mol)	ΔH° (J/mol)	ΔS° (J/mol)	ΔG°(303) (KJ/mol)	ΔG°(313) (KJ/mol)	ΔG°(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

Table 3. Inhibition efficiency of A for the corrosion of Zn in 0.01M H₂SO₄

Con (mol/dm ³)	Gasometric methods (2.5M H ₂ SO 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

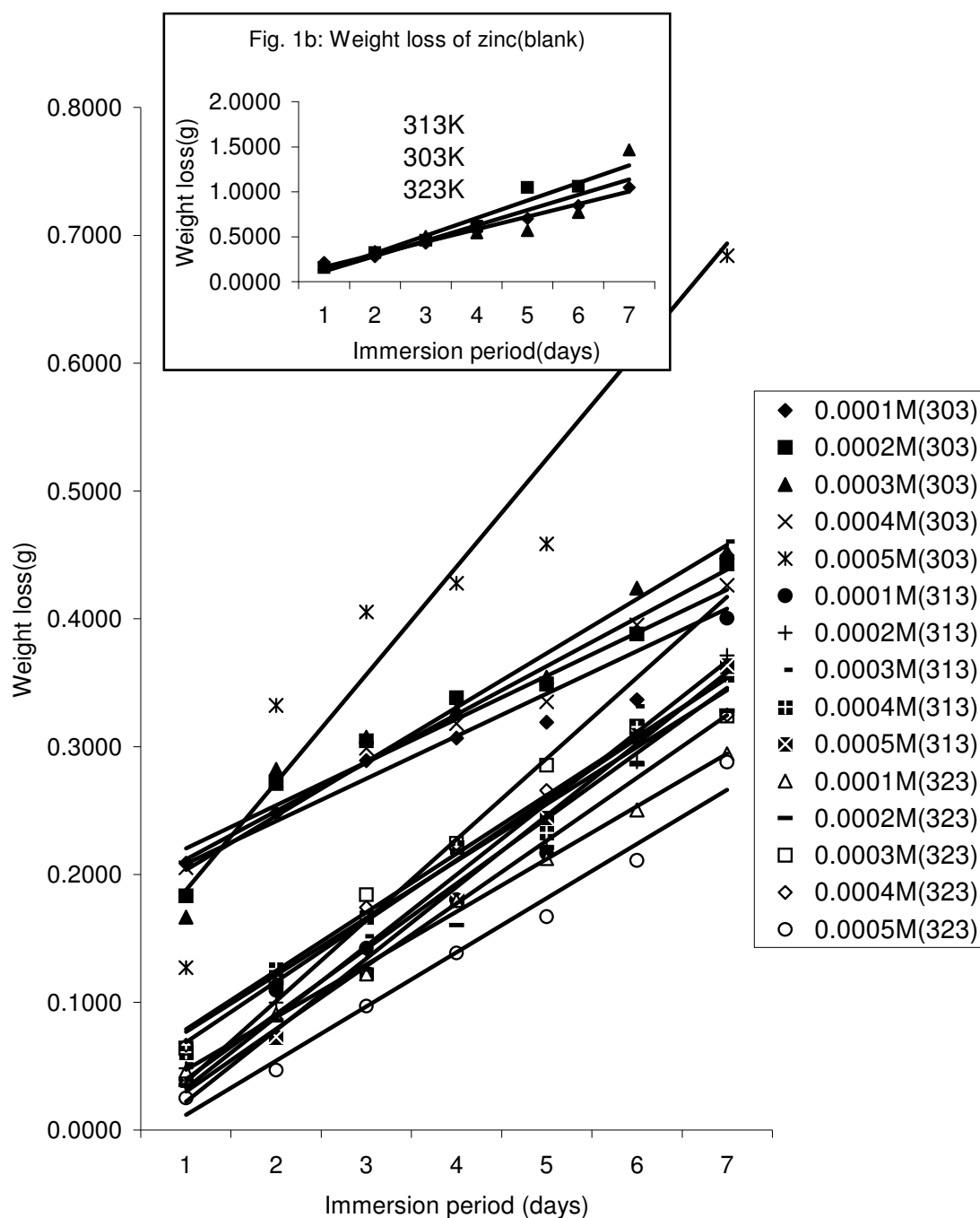


Fig. 1: Weight loss of zinc in 0.1M tetraoxosulphate (VI) acid in the presence of A

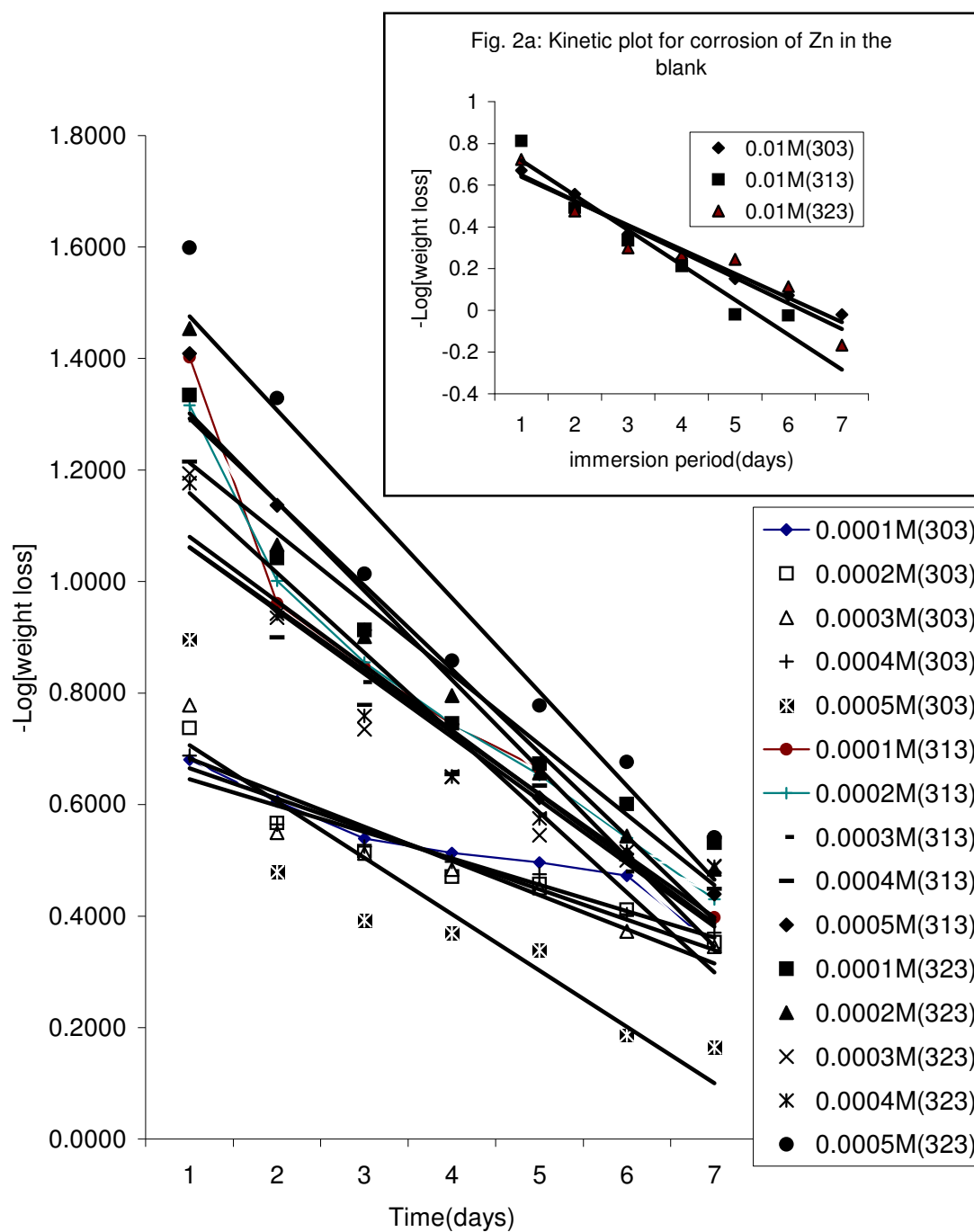


Fig. 2: Kinetic plot for the corrosion of Zn in 0.01M acid in the presence of A(insert, plot for the blank)

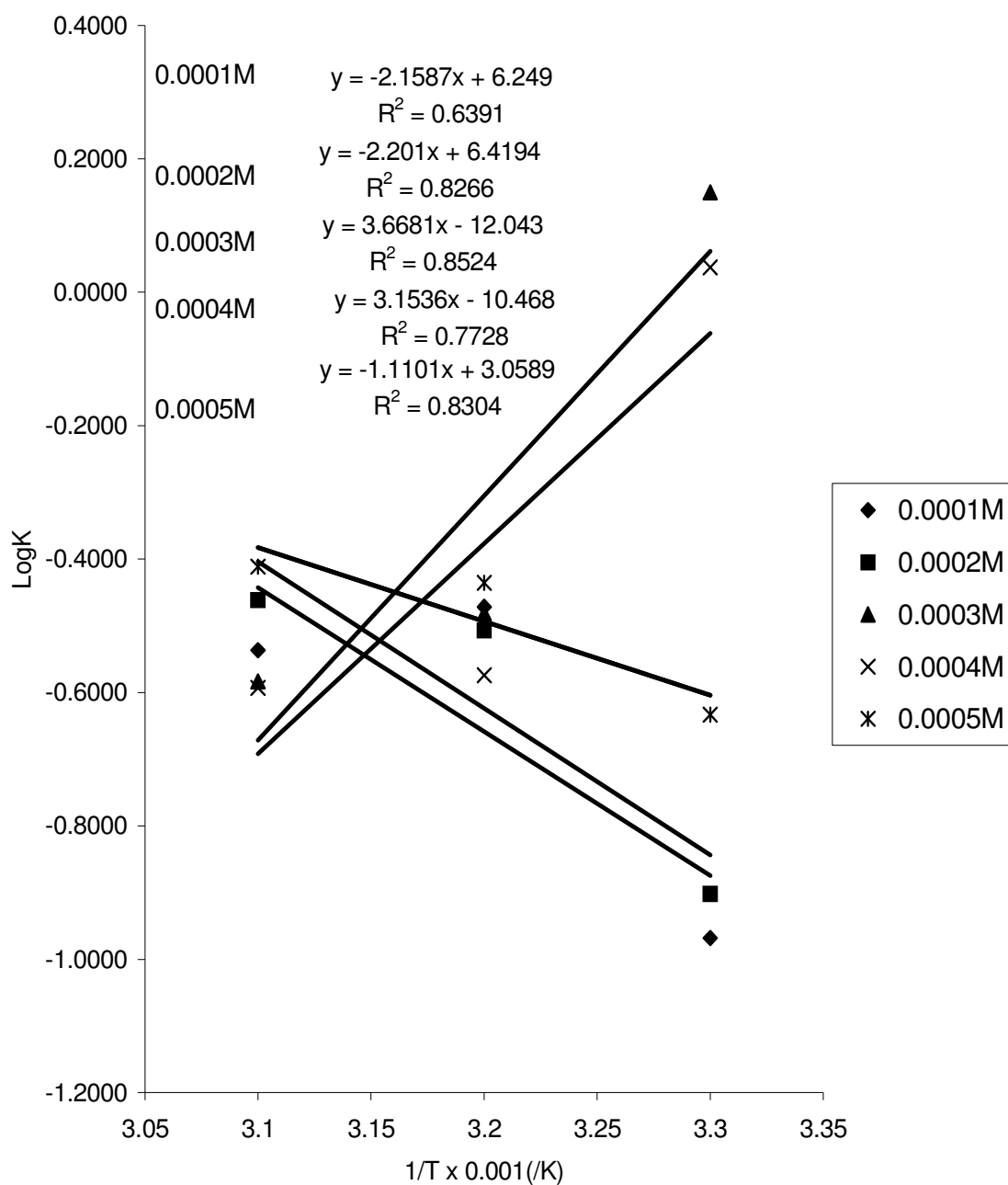


Fig. 3: Arrhenius plot for corrosion of zinc in 0.01M acid corrosion in the presence of A

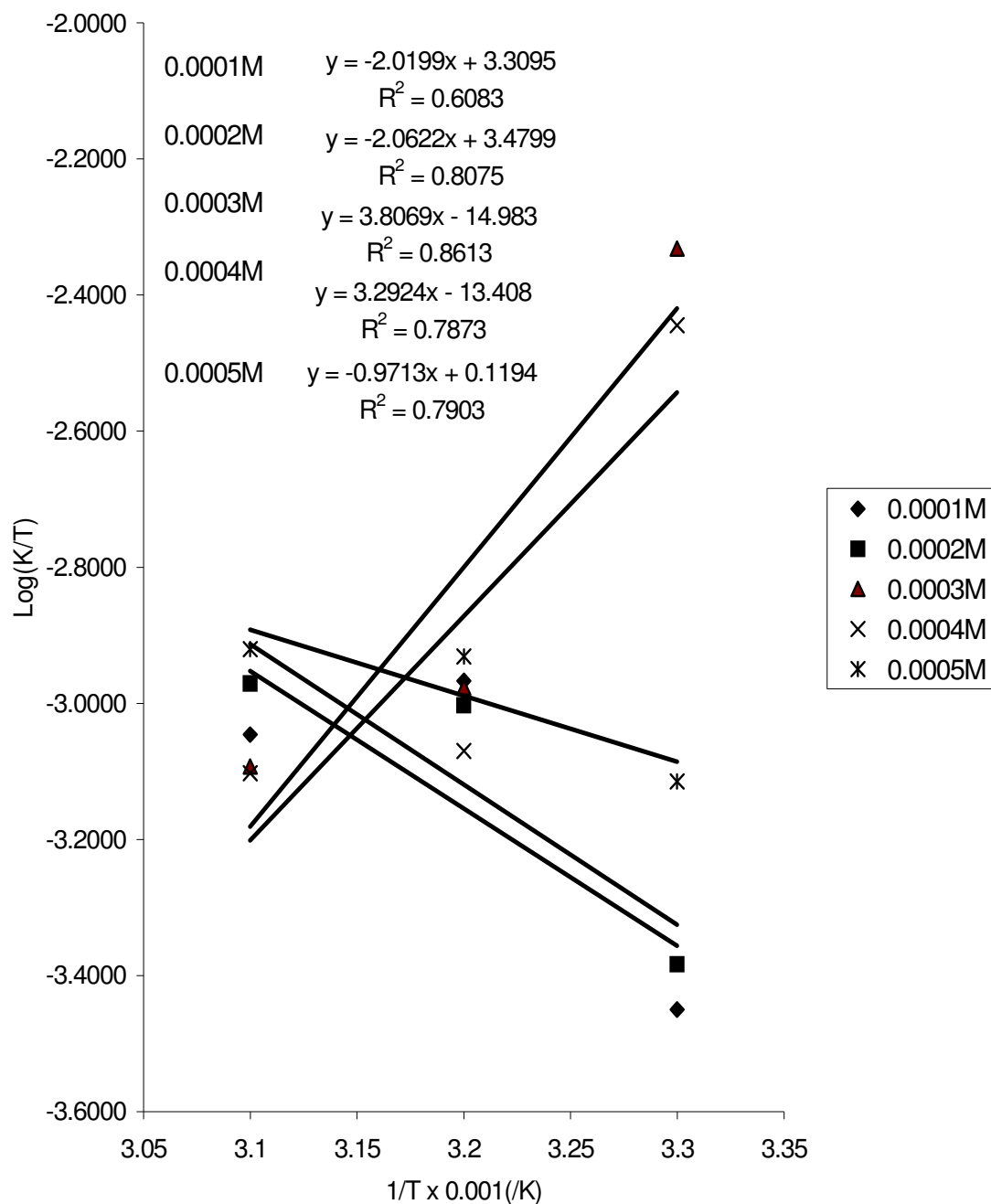


Fig. 4: Transition state plot for the corrosion of zinc in 0.01M acid in the presence of A

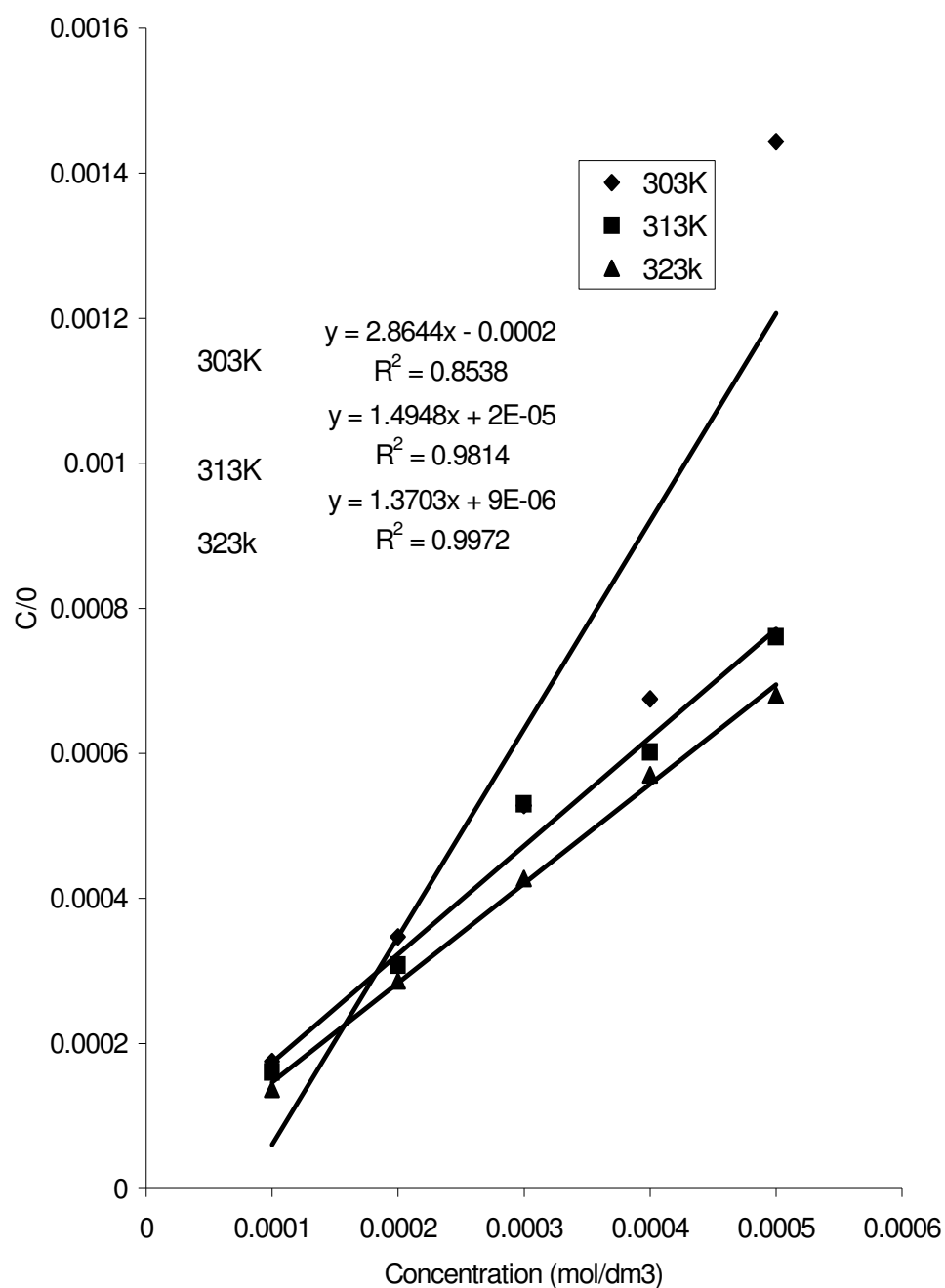


Fig. 5: Curve fitting for adsorption of sparfloxacin on mild Zn according to Lagmuir

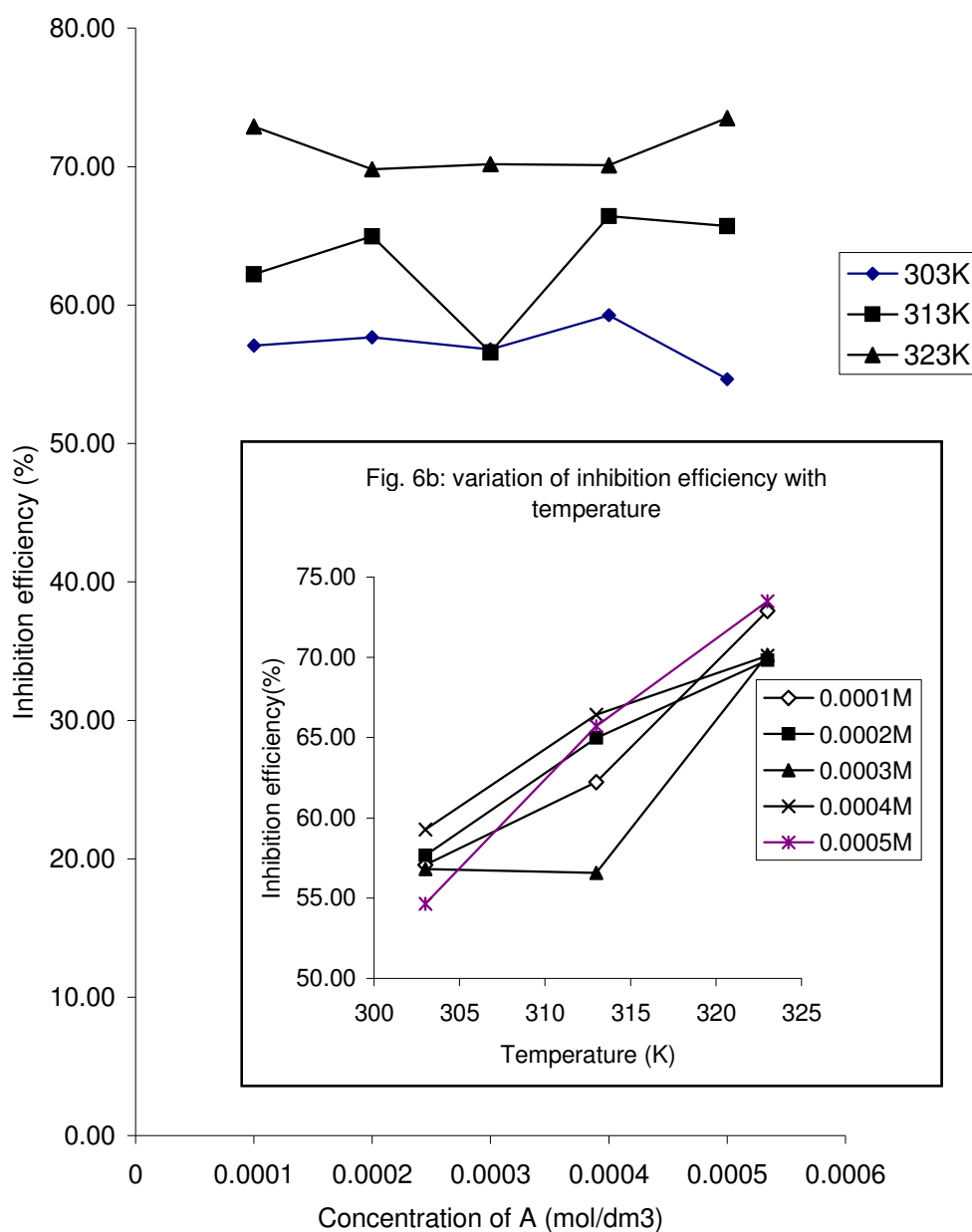


Fig. 6: Variation of inhibition efficiency of A with concentration of A