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Inhibition of corrosion of mild steel by 7-[2-amino-2-(4-hydroxyphenyl)-acetyl]amino-3,3-dimethyl-6-oxo-2-thia-5-azabicyclo[3.2.0]heptane-4-carboxylic acid

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ABSTRACT

7-[2-amino-2-(4-hydroxyphenyl)-acetyl]amino-3,3-dimethyl-6-oxo-2-thia-5-azabicyclo[3.2.0]heptane-4-carboxylic acid has been found to inhibit the corrosion of mild steel in 2.5M H₂SO₄. Inhibition efficiency of different concentrations of A(0.1-0.5g/dm³) ranged between 34.79-52.30 and 7.49-24.23 at 303 and 333K respectively. Mechanism of inhibition of mild steel corrosion by A is through spontaneous physical adsorption process($\Delta G_{ads} = -0.8853$ and -3.7274 KJ/mol at 303 and 333K respectively). Adsorption of A on mild steel surface is endothermic($\Delta H_{ads} =$ positive) and is characterized by high and positive values of ΔS_{ads} indicating the formation of a stable complex. © 2007 Trade Science Inc. - INDIA

KEYWORDS

Corrosion of iron;
Effect of A.

INTRODUCTION

The use of a corrosion inhibitor is one of the best option of protecting metals against corrosion^[1-3]. A corrosion inhibitor is any substances which when added in minute concentration, can retard/inhibit the rate of corrosion of a metal^[1-4].

The choice of an inhibitor is based on two options. First it can be synthesized from cheap raw materials. Secondly, it may be chosen from organic compound having hetero atom(N,S,O,P) in their long carbon chain or aromatic ring structure^[4-6]. Based on these, several inhibitors have been used for the protection of metal against corrosion^[7-9]. However, most of these inhibitors contain heavy metals or toxic compounds which

have the tendency of affecting the quality of the environment^[10-12]. The compound 7-[2-amino-2-(4-hydroxyphenyl)-acetyl] amino-3,3-dimethyl-6-oxo -2-thia-5-azabicyclo[3.2.0]heptane -4-carboxylic acid(A), meets the structural requirements for used as a corrosion inhibitor. It does not contain heavy metal or other toxic compounds. These properties suggest that A may be a good inhibitor that meets environmental and industrial requirements for green corrosion inhibitors.

The present study seeks to investigate the inhibitive properties of A for mild steel corrosion in H₂SO₄.

MATERIALS AND METHODS

Materials

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Materials used for the study were mild steel sheets of composition (wt%) Mn(0.6), P(0.36), C(0.15) and Si(0.03). The sheet was mechanically pressed cut to different coupons of dimension, $5 \times 4 \times 0.11$ cm. Each coupon was washed with ethanol, dried in acetone and preserved in a desiccator. All reagents used for the study were analar grade. Double distilled water was used for the preparation of 1-3M H_2SO_4 . The inhibitor (A) was supplied by Nnabuk Okon Eddy and the concentration range of A prepared for used was 0.1-0.5g/dm³. Each concentration was dissolved in 2.5M H_2SO_4 .

EXPERIMENTAL

Gasometric method

Gasometric methods were carried out at 303 and 333K as described in literature^[6-7]. From the volume of hydrogen evolved per minutes, inhibition efficiency (%I), and degree of surface coverage (θ) were calculated using equation 1 and 2 respectively.

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

$$\theta = \%I/100 \quad (2)$$

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.

Thermometric method

This was also carried out as reported elsewhere^[8-10]. From the rise in temperature of the system per minutes, the reaction number (RN) was calculated using equation 3:

$$RN(\text{°C minutes}) = \frac{T_m - T_i}{t} \quad (3)$$

where T_m is the maximum temperature attained by the system, T_i is the Initial temperature and t is the time. From the above, the inhibition efficiency of the used inhibitor was computed using equation 4:

$$\%I = \frac{RN_{aq} - RN_{wi}}{RN_{aq}} \times 100 \quad (4)$$

Where RN_{aq} and RN_{wi} are the reaction number in the absence and presence of the inhibitor respectively.

RESULTS AND DISCUSSION

Results

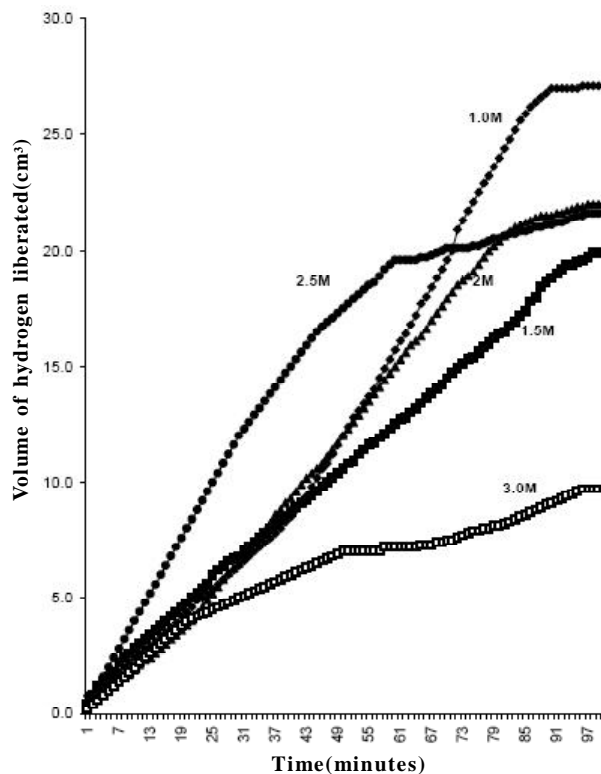


Figure 1: Gasometric plot for the corrosion of mild steel in different concentration of H_2SO_4 at 303K

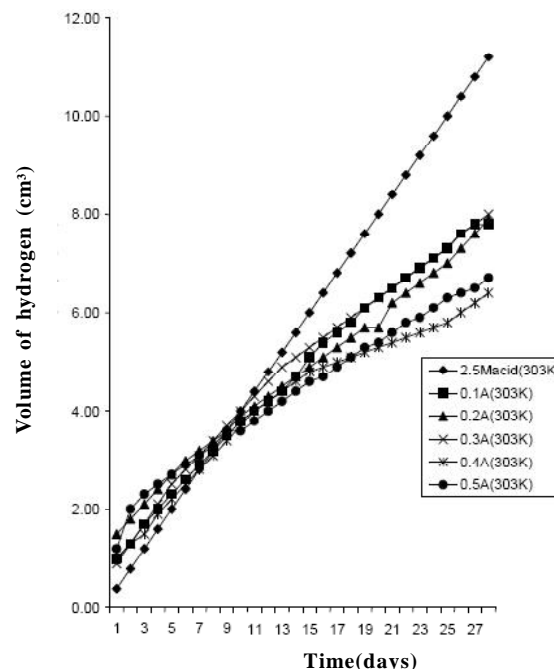


Figure 2: Gasometric plot for (A) at 303K

Figure 1 shows gasometric plot for the corrosion of mild steel in different concentration of H_2SO_4 . Figure 2 shows gasometric plot for the corrosion of mild

steel in 2.5M H₂SO₄ in the presence of different concentrations of (A) (0.1-0.5g/dm³) at 303k. Figure 3 shows gasometric plot for the corrosion of mild steel in the presence of different concentrations of (A) at 333k.

Discussion

From figure 1, it can be seen that the corrosion rate of mild steel is concentration dependents. The corrosion rate also increases with increase in the period of immersion of the mild steel. From figures 2 and 3, it is seen that addition of different concentration of (A) to 2.5M H₂SO₄ lowers the corrosion rate of mild steel indicating that (A) inhibits mild steel corrosion. Values of inhibition efficiency of (A) calculated from equation 1 are recorded in TABLE 1. From the results, it is noted that the inhibition efficiency of (A) is temperature and concentration dependents. At fixed concentration of (A), inhibition efficiency of (A) decrease with temperature but at constant temperature, variation of inhibition efficiency with concentration follows the trend, 0.1>0.4>0.3>0.2>0.5g/dm³ at 303K and 0.2>0.3>0.5>0.4>0.1g/dm³ at 333K.

Values of inhibition efficiency obtained from thermometric method are also recorded in TABLE 1. These values correlated strongly with values obtained from gasometric method ($r=0.8812$, $n=4$, $\alpha=0.05$) confirming that A inhibit mild steel corrosion.

In order to calculate the heat of adsorption of the inhibitor on mild steel surface, equation 5 was used^[10]:

$$Q_{ads} = 2.303R(\log\theta_2/1-\theta_2 - \log(\theta_1/1-\theta_1))(T_1T_2/T_2 - T_1) \quad (5)$$

where Q_{ads} is the heat of adsorption, R is the gas constant, θ_2 and θ_1 are the degree of surface coverage at temperature, T_2 (333K) and T_1 (303K) respectively. Values of Q_{ads} calculated from equation 5 were negative and ranged from 14.3146-72.0490KJ/mol (mean= 47.5520KJ/mol) indicating that the corrosion reaction of mild steel in the presence of (A) is endothermic (Sharma and Sharma, 2004).

According to Yurt et al.^[11], adsorption isotherms provide important clues about the nature of metal-inhibitor interaction. Frequently used adsorption isotherms are Lagmuir, Temkim, Freundlich, Bockris- Swindles, Florry Huggins and Frumppkin isotherms with general formula expressed by equation 6^[2]:

$$f(0,x) \exp(-2a\theta) = KC \quad (6)$$

where $f(0,x)$ is configuration factor, θ is the degree of surface coverage; C is inhibitors concentration; K is adsorption con-

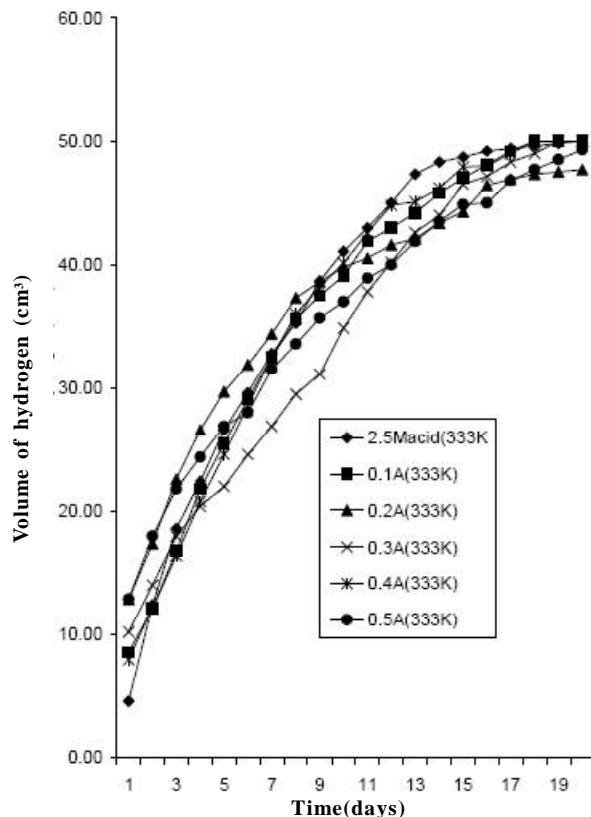


Figure 3 : Gasometric plot for (A) at 333K

stant and a is the molecular interaction parameter.

Attempt has been made to fit data obtained from hydrogen evolution measurements (at 303 and 333K) to different adsorption isotherm. By far the best isotherm that described the adsorption of (A) on mild steel surface is Frumkin adsorption isotherm. Assumptions of frumkin adsorption isotherm relates θ to inhibitor's concentration according to equation 7^[12-13]:

$$\log(\theta/1-\theta)[C] = \log K + 2\alpha\theta/2.303 \quad (7)$$

where α is interaction parameter and K is the equilibrium constant of adsorption. From equation 4.3, a plot of $\log(\theta/1-\theta)[C]$ versus θ should give a straight line with slope equal to $2\theta/2.303$ if the assumptions of Frumkin are applicable. Figure 4 shows Frumkin plot for the adsorption of (A) on mild steel surface. Values of α obtained from Frumkin plots (Figure 4) are 1.7855 and 3.5254 at 303 and 333K respectively. These values are positive and increase with temperature indicating that the magnitude of the attractive behaviour of A on mild steel surface increases with temperature.

The equilibrium constant of adsorption (equation 7) is related to the free energy (ΔG_{ads}) of adsorption ac-

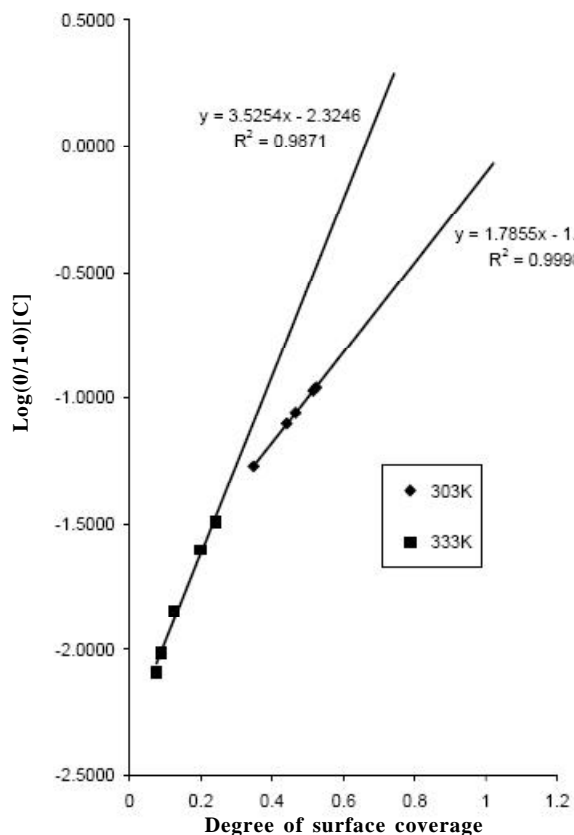


Figure 4: Curve fitting for adsorption of (A) on mild steel surface according to Frumkin adsorption isotherm

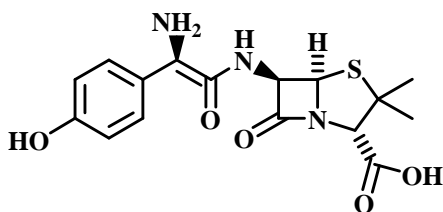


Figure 5: Chemical structure of (A)

According to equation 8^[13]

$$\Delta G_{\text{ads}} = -2.303RT \log (55.5K) \quad (8)$$

All parameters in equation 8 are as defined earlier,

TABLE 1: Values of inhibition efficiency and thermodynamic parameters of adsorption of A on mild steel surface

Con. (g/dm ³)	%I (303K)	%I (333K)	%I (thermometric)	Q _{ads} (KJ/mol)
0.1	52.30	8.82	33.34	67.9017
0.2	34.79	24.23	16.67	14.3146
0.3	44.10	12.33	33.34	48.2283
0.4	51.56	7.49	33.34	72.0490
0.5	46.59	19.82	-	35.2662
ΔG _{ads} (KJ/mol)	-0.8853	-3.7274		
ΔS _{ads} (KJ/mol)	3.0788	11.3362		

values of ΔG_{ads} calculated through equation 8 are recorded in TABLE 1. The negative values of ΔG_{ads} indicates that the adsorption of (A) on mild steel surface is spontaneous and is governed by mechanism of physical adsorption ($\Delta G_{\text{ads}} < -40\text{KJ/mol}$)^[14-18]:

Values of entropy of adsorption were calculated using the Gibb-Helmholtz equation^[16-17]:

$$\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\Delta S_{\text{ads}} \quad (9)$$

Rearranging equation 8, equation 10 is obtained:

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

Values of ΔS_{ads} calculated through equation 10 were positive indicating the formation of a compact activation complex rather than dissociation^[1].

The structural formula of (A) is shown by Figure 5. In dilute acid, (A) (structure I) undergoes hydrolysis to give structure II (Figure 6). Breaking of double bonds in the carboxylic acid functional group (structure I) leaves the compound with free electrons which are donated to vacant d-orbital of mild steel to form a stable complex (structure III).

The proposed mechanism is supported by moderate values of activation energy and other observable thermodynamics parameters (ΔH_{ads} , ΔG_{ads} and ΔS_{ads}). The fairly high positive value of enthalpy of adsorption of (A) by mild steel surface indicates that the inhibition

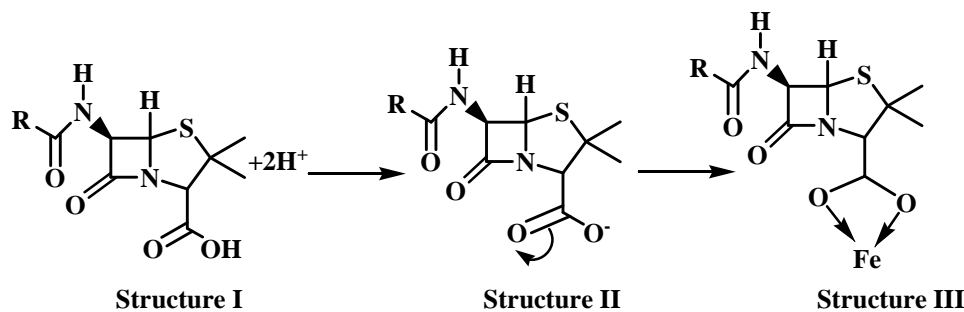


Figure 6: Mechanism of inhibition by A, B, and C

of mild steel corrosion is highly solvated while the high negative values of entropy of adsorption indicates the formation of a compact activated complex (as each inhibitor donates its electrons to the vacant d orbital of iron) with fewer degree of freedom^[19-21].

CONCLUSION

From the foregone study, the following conclusions are drawn,

- i. The corrosion of mild steel in H_2SO_4 depends on concentration and temperature.
- ii. Different concentrations of (A) is capable of inhibiting mild steel corrosion in 2.5m H_2SO_4 . Values of inhibition efficiency of (A) varies with concentration and temperature. Optimum values of inhibition efficiency of (A) were obtained at room temperature (303K). At 333K, forces of desorption tends to lower values of inhibition efficiency of (A).
- iii. Thermodynamic considerations reveal that adsorption of (A) on mild steel surface is feasible and a formation of a compact activated complex is eminent.
- iv. Physical adsorption mechanism is proposed for the adsorption of (A) according to classical isotherm of Frumkin.

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