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Inhibitive and Adsorptive Properties of Orphenadrine for the Corrosion of Mild Steel in H_2SO_4

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Abstract: Inhibitive and adsorption properties of orphenadrine for the corrosion of mild steel in 2.5M H_2SO_4 have been studied using hydrogen evolution and thermometric methods. Orphenadrine inhibited the corrosion of mild steel in H_2SO_4. Inhibition efficiency of orphenadrine was found to increase with increase in concentration of orphenadrine but decreases with increase in temperature. Thermodynamic consideration revealed that values of activation energy for the inhibited corrosion were higher than the value obtained for the blank solution. Calculated values of enthalpy and free energy change revealed that the adsorption of orphenadrine on mild steel surface is exothermic and spontaneous. Based on values of activation energy and free energy of adsorption, a physical adsorption mechanism has been proposed for the adsorption of orphenadrine on the surface of mild steel. Langmuir and Frumkin adsorption isotherms described the adsorption behaviour of orphenadrine on the surface of mild steel.

Key word: Corrosion of mild steel, inhibition, orphenadrine

INTRODUCTION

The use of an inhibitor during industrial processes such as acid cleaning, prickling, descaling, etching etc has proven to be one of the best methods of protecting metals against corrosion (Ashassi-Sorkhabi, H. and N. Ghalebsaz-Jeddi, 2005. Emregul, K.C. and O. Atakol, 2003). This implies that a search for a good inhibitor is imperative. Most inhibitors in use are either synthesized from cheap raw materials or are organic compounds containing hetero-atoms in their aromatic system or long carbon chain (Abdallah, M., 2002. Abdallah, M., 2004).

Establishing the suitability of any inhibitor involves application of kinetic, thermodynamic and adsorption principles (Odoemelam, S.A. and N.O. Eddy, 2008. Kumar, A., 2008). Also, it has been established that the initial step involves in most inhibitors' action is the adsorption of the inhibitor on the surface of the metal (Abdallah, M., 2004. Odoemelam, S.A. and N.O. Eddy, 2008). Based on this, several inhibitors have been utilized to protect metals against corrosion. However, to the knowledge of the author, the used of orphenadrine as an inhibitor for the corrosion of mild steel in H_2SO_4 has not been reported elsewhere. Therefore, the study is aimed at studying adsorptive and inhibitive properties of orphenadrine for the corrosion of mild steel in H_2SO_4.

MATERIALS AND METHOD

Materials used for the study were mild steel sheet of composition (wt %) Mn (0.6), P(0.36), C(0.15) and Si(0.03). The sheet was mechanically pressed cut to form different coupons, each of dimension, 5x4x0.11cm. Each coupon was degreases by washing with ethanol, dried in acetone and preserved in a desiccator. All reagents used for the study were analar grade and double distilled water was used for their preparation. The inhibitor used for the study was manufactured by PubChem companay, Germany.

Gasometric method:

Gasometric methods were carried out at 303 and 333K as described in literature. (Oguzie, E.E., 2006. Umoren, S.A., *et al.,* 2006). From the volume of hydrogen evolved per minutes, inhibition efficiency (%I), and degree of surface coverage (θ) were calculated using Equations 1 and 2 respectively.

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

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$$\theta = \eta/100 \tag{2}$$

Thermometric method:

This was also carried out as reported elsewhere. [8-9] From the rise in temperature of the system per minutes, the reaction number (RN) was calculated using Equation 3:

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

RESULTS AND DISCUSSION

Fig. 1: shows the variation of volume of hydrogen gas evolved with time during the corrosion of mild steel in various concentrations of H_2SO_4. From the Figure, it is seen that the rate of corrosion of mild steel in H_2SO_4 increases with increase in the concentration of the acid.

Figs. 2: and 3 show the variation of volume of hydrogen gas evolved with time during the corrosion of mild steel in 2.5M H_2SO_4 containing various concentrations of orphenadrine at 303 and 333K respectively. From the Figures, it is seen that the volume of hydrogen gas evolved increases with time and temperature but decreases as the concentration of the orphenadrine increases indicating that the rate of corrosion of mild steel in H_2SO_4 increases as the period of contact and temperature increase but decreases as the concentration of orphenadrine increases. This also suggests that orphenadrine inhibits the corrosion of mild steel and its inhibition efficiency increases with its concentration but decreases with increase in temperature.

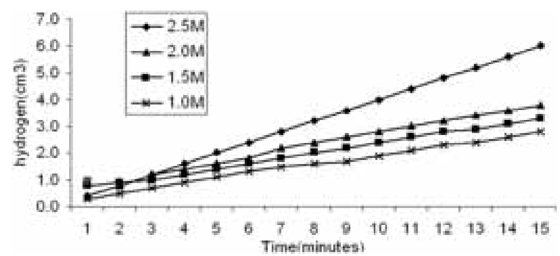

Fig. 1: Variation of hydrogen gas evolved with time for the corrosion inhibition of mild steel at various concentrations of methocarbamol at 303K.

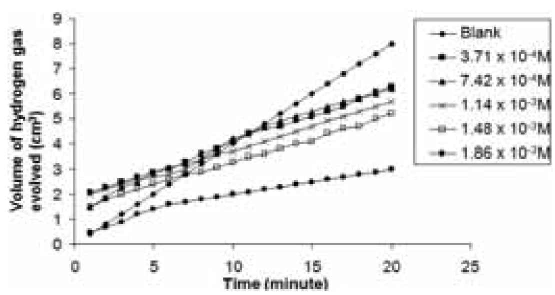

Fig. 2: Variation of volume of hydrogen gas evolved with time or the corfrosion of mild steel in 2.5M tetraoxosulphate (VI) containing various concentrations of orphenadrine at 303K.

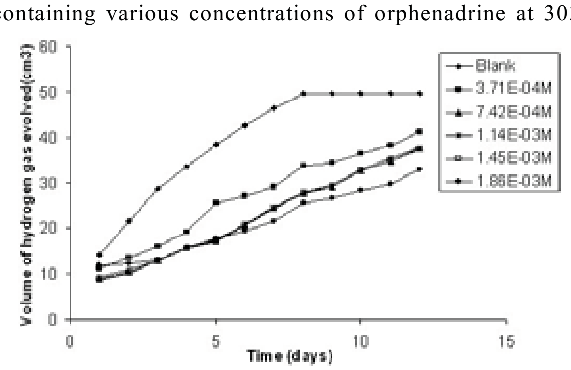

Fig. 3: Variation of the volume of hydrogen gas evolved with time for the corfrosion of mild steel in 2.5M tetraoxosulphate (VI) containing various concentrations of orphenadrine at 333K.

Values of corrosion rates, reaction number and inhibition efficiency of orphenadrine for the corrosion of mild steel in the absent and presence of different concentrations of orphenadrine are recorded in Table 1. From the results, it is seen that at 303K, the corrosion rates of mild steel in H_2SO_4 decreases as the concentration of orphenadrine increases but increases with increase in temperature indicating that the inhibition efficiency of orphenadrine increases with its concentration but decreases with increase in temperature.

Values of inhibition efficiency of orphenadrine obtained from thermometric method were relatively higher than values obtained from hydrogen evolution measurement. However, both data correlated strongly with each other ($P \geq 0.05$) confirming that orphenadrine is a good inhibitor for the corrosion of mild steel.

In other to predict the effect of temperature on the corrosion of mild steel in the absent and presence of orphenadrine as an inhibitor, Arrhenius equation was used. The expression of Arrhenius equation can be written as follow (Umoren, S.A., *et al.,* 2006. Eddy, N.O. and A.S. Ekop, 2008).

$$CR = A\exp(-E_a/RT) \qquad (4)$$

where CR is the corrosion rate of mild steel, A is the Arrhenius or pre-exponential factor and T is the temperature. Taking logarithm of both sides of Equation 4, Equation 5 is obtained,

$$\log CR = \log A - E_a/2.303RT \qquad (5)$$

Given that the corrosion rate of mild steel at 303K (T_1) and 333K (T_2) are CR(303K) and CR(333K), then Equation 5 can be written as,

$$\log \frac{CR(333K)}{CR(303K)} = E_a/2.303R \frac{(T_2 - T_1)}{T_1T_2} \qquad (6)$$

Values of E_a calculated through Equation 6 are recorded in Table 2. The values ranged from 63.8912 to 74.8330KJ/mol. These values are greater than the value obtained for the blank (55.67KJ/mol) indicating that the corrosion of mild steel is retarded by different concentrations of orphenadrine. These values are also lower than threshold value (80KJ/mol) required for chemical adsorption indicating that orphenadrine inhibits mild steel corrosion via physical adsorption mechanism.

The heat adsorbed (Q_{ads}) during the inhibition of the corrosion of mild steel by orphenadrine was calculated using Equation 7(Oguzie, E.E., 2006).

$$Q_{ads}=2.303R[\log(\theta_2/1-\theta_2) - \log(\theta_1/1- \theta_1) \times (T_2T_1)/(T_2 - T_1) \qquad (7)$$

Table 1: Values of inhibition efficiency, corrosion rate and reaction number during the inhibition of the corrosion of mild steel in H_2SO_4 by various concentrations of orphenadrine

Concentration of orphenadrine (M)	Inhibition efficiency			CR (cm^3/min)		RN(°C/min)
	Gasometric		Thermometric			
	%I(303K)	%I(333K)	%I(303K)	CR(303)	%I(333K)	RN
3.71×10^{-4}	35.53	18.59	84.62	0.245	18.59	0.030
7.42 x 10-4	44.74	20.41	84.62	0.210	20.41	0.030
1.14×10^{-3}	51.32	20.86	87.18	0.185	20.86	0.025
1.48×10^{-3}	51.32	22.00	87.18	0.185	22.00	0.025
1.86×10^{-3}	67.11	38.55	89.75	0.125	38.55	0.020

Table 2: Some thermodynamic and adsorption parameters for the adsorption of orphenadrine on mild steel surface.

Concentration of orphenadrine (mol/dm^3)	E_a (KJ/mol)	DH_{ads} (KJ/mol)
3.71×10^{-4}	63.8912	-18.4806
7.42 x 10-4	67.4983	-24.1153
1.14×10^{-3}	70.9272	-29.0764
1.48×10^{-3}	70.4424	-27.6559
1.86×10^{-3}	74.8330	-24.7393

where R is the gas constant, q_1 and q_2 are the degree of surface coverage at temperatures, T_1 and T_2 respectively. It should be noted that since the process was carried out at constant pressure, the heat adsorbed should be equal to the enthalpy change (Atkins, P., 2002. Sharma, K.K. and L.K. Sharma, 2004). Values of Q_{ads} calculated from Equation 7 are recorded in Table 2. The values ranged from -18.4806 to -24.7393KJ/mol indicating that the adsorption of orphenadrine on the surface of mild steel is exothermic.

Values of degree of surface coverage calculated from hydrogen evolution measurements have been used to study the adsorption characteristics of orphenadrine on the surface of mild steel. The data obtained within the temperature range of 303 and 333K were used to fit curves for different adsorption isotherms including Langmuir, Flory-Huggins, Frumkin, Temkin, Freundlich and El awardy isotherms. By far, the data best fitted

Langmuir and Frumkin adsorption isotherms. The assumptions of Langmuir adsorption isotherm is represented by Equation 7 (Umoren, S.A., *et al.,* Eddy, N.O. and A.S. Ekop, 2008).

$C/\theta = 1/k + C$ (8)

Rearranging and taking logarithm of both sides of Equation 8, Equation 9 is obtained

$\log(C/\theta) = \log C - \log K$ (9)

By plotting values of C/q versus C (Fig. 4), linear plots were obtained confirming the applicability of Langmuir adsorption isotherm to the adsorption of orphenadrine on the surface of mild steel at 303 and 333K. Therefore there is no interaction between the adsorbed species.

Adsorption of orphenadrine on mild steel surface also occured according to Frumkin isotherm (Equation 10):

$\log([C] *(\theta/(1-\theta)) = 2.303\log K+2\alpha\theta$ (10)

where K is the adsorption-desorption equilibrium constant and a is the lateral interaction term describing the molecular interaction in adsorbed layer (Atkins, P., 2002. Ebenso, E.E., 2003). Fig. 5 shows Frumkin plots for adsorption of ampiclox on mild steel surface. Values of Frumkin adsorption parameters are also recorded In Table 3. From the results, values of a were found to be positive indicating the attractive behaviour of ampiclox on the surface of mild steel (Ashassi-Sorkhabi, H. and N. Ghalebsaz-Jeddi, 2005).

The free energy of adsorption DG_{ads}) of orphenadrine on mild steel surface is related to the equilibrium constant of adsorption according to Equation 11 (Umoren, S.A., *et al.,* 2006. Fouda, A.S., *et al.,* 2005).

$K = 1/55.5 \times \exp(-\Delta G_{ads}/RT)$ (11)

Taking logarithm of both sides of Equation 11, Equation 12 is obtained,

$\Delta_{gads} = -2.303RT\log(55.5K)$ (12)

Table 3: Values of adsorption constant and free energy of adsorption

Langmuir	Temperature (K)	logK	Slope	ΔG_{ads}	R^2
	333	0.7402	0.6515	-5.8253	0.9738
	303	0.3710	0.6664	-7.9673	0.8201
Frumkin	Temperature (K)	logK	α	ΔG_{ads}	R^2
	333	-5.0186	2.0049	-2.5229	0.9522
	303	-1.5926	1.5929	-6.1077	0.9495

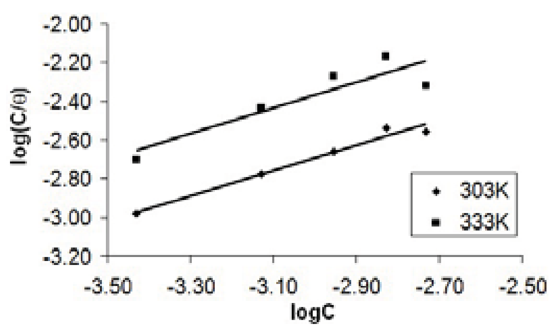

Fig. 4: Langmuir isotherm for adsorption of orphenadrine on mild steel surface.

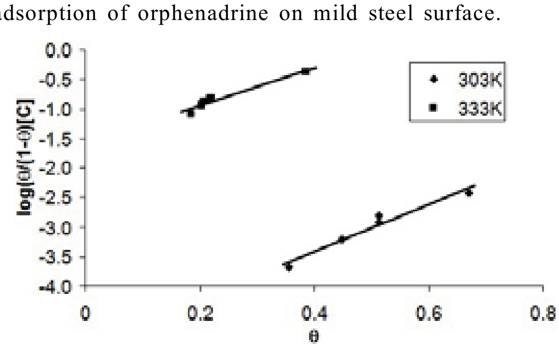

Fig.5: Frumkin isotherm for the adsorption of orphenadrine on mild steel surface.

where R is the gas constant, T is the temperature, K is the adsorption-desorption equilibrium constant and C is the concentration of the inhibitor. Values of ΔG_{ads} calculated from Equation 12 are recorded in Table 3. Calculated values of ΔG_{ads} were negative and lower than threshold value required for physical adsorption indicating that the adsorption of orphenadrine on the surface of mild steel is spontaneous and occur via physical adsorption mechanism (Ebenso, E.E., 2003). For a physical adsorption mechanism, the value of the free energy of adsorption should be more negative than -40.00KJ/mol therefore the data is consistent with those required for physical adsorption mechanism.

The chemical structure of orphenadrine is shown by Fig. 6. Its molecular formula is 269.3812g/mol. From the chemical structure, it can be seen that orphenadrine has $-NH_2$ as a functional group in addition to the presence of O suggesting that the inhibition efficiency of this compound is largely contributed by its chemical structure. Amino group present in orphenadrine is an electron releasing/donating group and is capable of releasing electron to vacant d-orbital of Fe^{2+}. Based on this, the author proposed the following mechanism for the inhibition of the corrosion of mild steel by orphenadrine. In acidic medium, the NH_2 substituent of orphenadrine undergoes ionization to form NH^- as shown by Fig. 7a. This leaves the orphenadrine system with one electron. Therefore each molecule orphenadrine donates an electron to a vacant d-orbital of iron leading to the formation of Fe-oprhandrine complex (Fig. 7b) which protect the metal against further corrosion. The proposed mechanism is supported by the high values of activation energy, enthalpy change which suggest the formation of a stable complex. The negative values obtained for free energy of adsorption indicates that the formation of this complex is spontaneous.

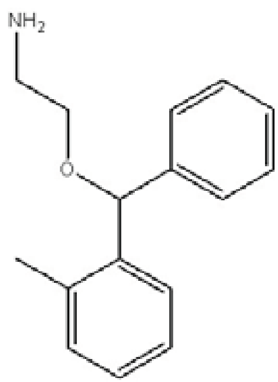

Fig. 6: Chemical structure of orphenadrine.

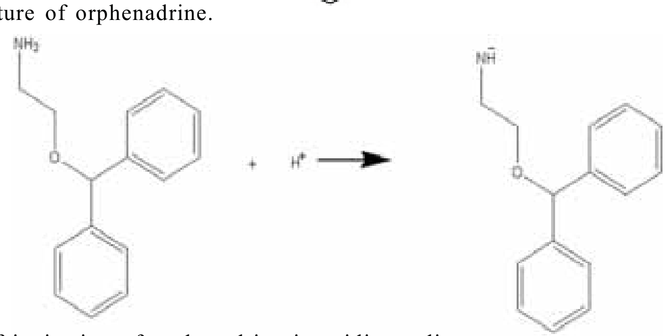

Fig. 7a: Mechanism of ionization of orphenadrine in acidic medium.

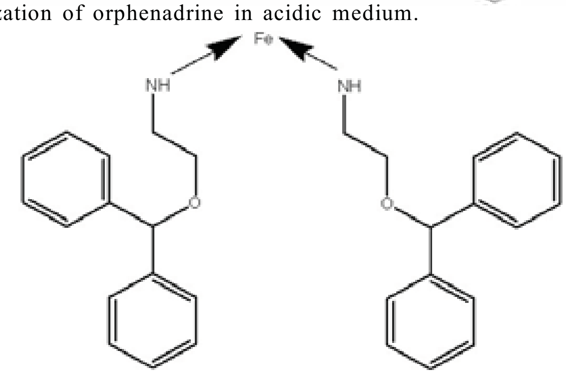

Fig. 7b: The formation of Fe-orphenadrine complex.

Conclusion:

The study reveals that orphenadrine is a good inhibitor for the corrosion of mild steel in H_2SO_4. The inhibitor acts by been adsorbed spontaneously on the surface of mild steel according to classical adsorption isotherm of Langmuir and Frumkin. Inhibitive and adsorption properties of orphenadrine for mild steel corrosion is affected by concentration of the inhibitor and temperature. The use of this compound as a corrosion inhibitor is hereby recommended.

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