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Inhibitory Action of Benzofuran Derivatives on Mild Steel Corrosion in Hydrochloric Acid Solutions

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Abstract

Derivatives of benzofuran ((E)-ethyl-5-(2-phenyldiazenyl) benzofuran-2-carboxylate and ethyl 5-aminobenzofuran-2-carboxylate) were used as corrosion inhibitors for mild steel in hydrochloric acid solution. The inhibition efficiency depended on the concentration and type of the benzofurans. The inhibition efficiency ranged between 75 and 85 % at the highest concentration (25 mM), and between 35 and 40 % at the lowest concentration (5 mM) of inhibitor in 1 M HCl solution. Inhibition efficiency decreased with rise in temperature, this corresponded to surface coverage of the metal by the inhibitor. Potentiodynamic polarization measurements have been carried out at room temperature, which clearly reveal the fact that all investigated inhibitors are of mixed type and they inhibit corrosion of mild steel by blocking the active sites of the metal surface. The results also showed that, the inhibitors were adsorbed on the mild steel surface according to Langmuir adsorption isotherm.

Keywords: Corrosion, Mild steel, Hydrochloric acid, Benzofurans, Langmuir adsorption, Temkin's adsorption isotherm.

Introduction

Acidization of petroleum oil and gas well is one of the important techniques for enhancing oil production. It is brought about by forcing a solution of 15-28% HCl into the well to open channels and to increase flow of oil and gas. Hydrochloric acid is the major acidizing agent. To reduce the corrosive attack of the acid, inhibitors are incorporated with the acid solution during the process of an acidization. The use of acid solution during pickling and industrial cleaning leads to corrosive attack on mild steel. Therefore, corrosion of mild steel and its inhibition in acidic solutions have attracted the attention of number of investigators¹⁻⁴. The protection of mild steel against corrosion can be achieved by adding a small concentration of organic compounds to environment⁵.

A survey of literature reveals that the applicability of organic compounds as corrosion inhibitors for mild steel in acidic media has been recognized for a long time. Compounds including aromatic amine⁶, aliphatic amine⁷, surfactants⁸, hydrazides⁹, organic dyes¹⁰⁻¹², drugs¹³,

poly (4-vinylpyridine)¹⁴, thiosemi-carbazide¹⁵ and heterocyclic compounds such as triazole¹⁶⁻¹⁷, bipyrazolic¹⁸, pierazine¹⁹, pyrazolones²⁰, thiazole²¹ and imidazoles²² were reported as inhibitors. Therefore, The present paper explain a study of corrosion protection action of benzofuran derivatives on mild steel corrosion in 1, 2 and 3M hydrochloric acid solution using weight loss and electrochemical techniques. Different concentrations of inhibitor were prepared and there inhibition efficiency in acidic media was investigated.

Experimental

Material Preparation

Mild steel contains Fe = 99.746; Mn = 0.100; C = 0.058; Al = 0.033; Si = 0.010; Cr = 0.008; Cu = 0.004; Ni = 0.0029; Mo = 0.002% were used in this study. Each sheet, which was 0.12 cm in thickness, was mechanically press-cut into coupons of dimension

3.5 x 3 cm with small hole of about 5 mm diameter near the upper edge. These coupons were used in the "as cut" condition, inhibition efficiency without further polishing, but were de-greased in absolute ethanol, dried in acetone, weighed and stored in a moisture-free desiccator prior to use.

All chemicals and reagents used were of analytical grade and used as source without further purification. The aggressive media were, respectively, 1, 2 and 3 M HCl solution. Benzofuran derivatives were used as inhibitor in the concentration range 5, 10, 15, 20 and 25 mM.

Gravimetric Method

Room Temperature

The test specimens were immersed in 1 to 3 M HCl solution with without inhibitors. Only one specimen was suspended by a glass hook, in each beaker containing 230 ml of the test solution and was open to air at room temperature for 24 h. After the immersion, the surface of the specimen was cleaned with double distilled water, followed by rinsing with acetone and the sample was weighed again in order to calculate inhibition efficiency (%). Triplicate experiments were performed in each case and the calculated mean values of the weight loss data are presented in figure 1.

Effect of Temperature

This experiment was done at temperatures 313, 323 and 333K. In this experiment, 250 ml beakers were used. The weighed mild steel coupon was inserted into a beaker containing 230 ml of 1M acid concentrations, with the help of a thread and was put in a thermo stated water bath. The coupons were removed after 3 hrs. The coupons were washed several times double distilled water with bristle brush, again rinsed with distill water and dried in acetone and then reweighted. This experiment was repeated with various concentrations of inhibitor in 1M HCl.

The differences in weight of the coupons were taken as the weight loss which was used to compute the corrosion rate by given relationships;

$$\text{Corrosionrate}(mpy) = \frac{543w}{rAt} \quad (1)$$

Where W is weight loss (g), r is the density of specimen (gcm^{-3}), A is surface area of the specimen (cm^2) and t is the exposure time (days). The inhibition efficiency of piperazine derivatives were calculated using the expression:

$$y\% = \left(\frac{W_0 - W_1}{W_0} \right) \times 100 \quad (2)$$

Where W_0 and W_1 are the weight loss of mild steel in the absence and presence of inhibitor in HCl medium at the same temperature. The degree of surface coverage (θ) was also calculated using the equation:

$$\theta = \left(\frac{W_0 - W_1}{W_0} \right) \quad (3)$$

Inhibition efficiency (%), energy of activation (E_a), heat of adsorption (Q_{ads}), free energy of adsorption (G^o_{ads}), enthalpy of adsorption (H^o_{ads}) and entropy of adsorption (S^o_{ads}) were calculated.

Polarisation Studies

For polarization study, metal specimens having an area of 0.25 cm^2 were exposed to corrosive solutions. Mild steel was used as a working electrode, SCE was used as reference electrode and auxiliary graphite electrode was placed in 100 ml of corrosive media through which external current was supplied automatically from computerized polarization instrument. The change in potential was measured by potentiostate/galvanostate (Gamry-Make, USA) on potentiostate mode with 5 mV/s scan rate. Polarization study was done with and without inhibitors in 1.0 M HCl.

Results and Discussion

The results are presented in Tables 1 to 2 and Figs. 1 to 10. To assess the corrosion rate of mild steel in HCl with and without benzofuran derivatives. The corrosion rate of mild steel in HCl was increased with the acid concentration which was depicted in figure 1.

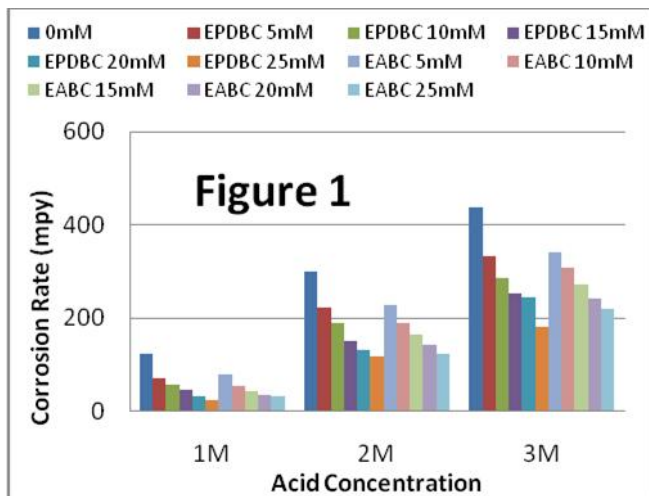


Figure 1: Corrosion rate of mild steel in HCl with and without inhibitors for 24 h at 301 K.

At constant inhibitor concentration, the inhibition efficiency decreased with the increase in acid concentration. At 25 mM inhibitor concentration, the inhibition efficiency of (E)-ethyl-5-(2-phenyldiazenyl) benzofuran-2-carboxylate was 80.39, 60.21 and 58.60 with respect to 1.0, 2.0 and 3.0 M acid concentrations respectively. At constant acid concentration, the

inhibition efficiency of the (E)-ethyl-5-(2-phenyldiazenyl) benzofuran-2-carboxylate increased with the inhibitor concentration, e.g. with EPDBC in 1.0 M HCl the inhibition efficiency was found to be 42.48, 52.94, 62.75, 72.55 and 80.39 with respect to 5, 10, 15, 20 and 25 mM inhibitor concentrations respectively (Figure 2).

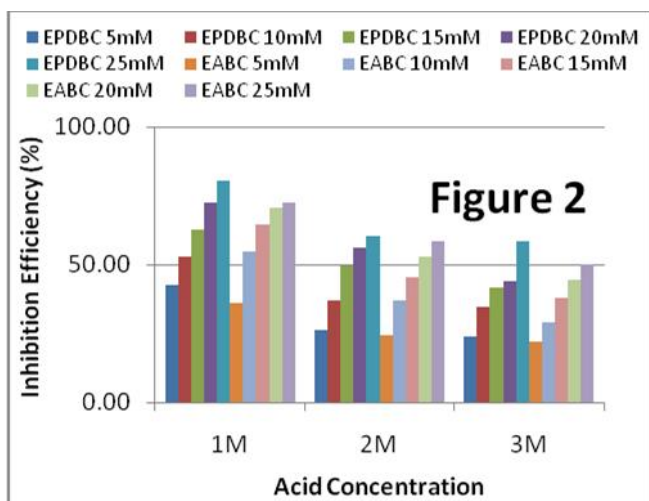


Figure 2: Effect of inhibition efficiency of Benzofurans for mild steel at different acid and inhibitor concentrations for 24 h at 301 K.

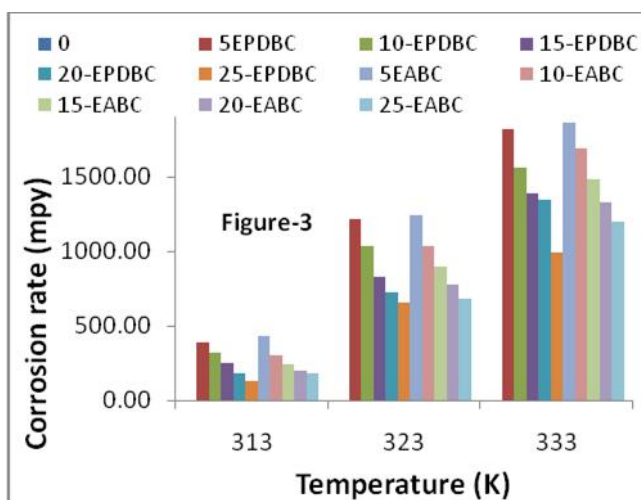


Figure 3: Corrosion rate of mild steel in HCl with & without inhibitors at various temperatures for 3h.

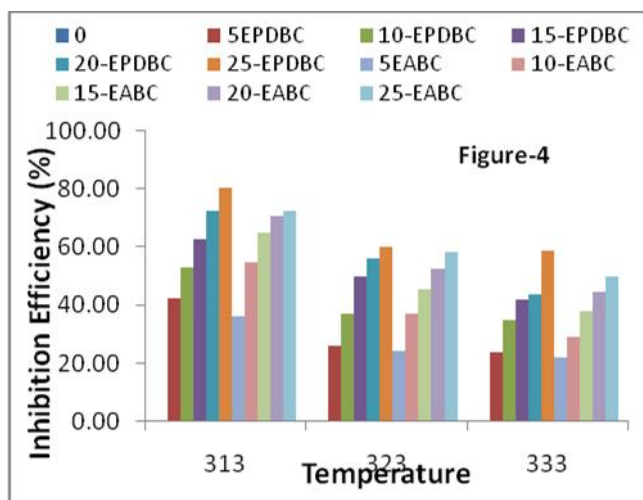


Figure 4: Effect of inhibition efficiency of benzofurans for mild steel in 1M HCl at various temperatures for 3h.

Temperature had significant influence on the metal corrosion rates. The effect of change in temperature on the corrosion rates of mild steel in 1.0 M HCl was examined. It was found that, the corrosion rate of mild steel increased with increase in temperatures (Figure 3). Corrosion rate was measured in 1.0 M HCl containing 5, 10, 15, 20 and 25mM inhibitor concentration at solution temperature of 313, 323 and 333 K for an immersion period of 3 h. It shows that the increase in corrosion rate may be due to the

adsorptions of the adsorbed molecules-inhibitor and /or aggressive at higher temperature and thus exposing the fresh metal surface to further attack which results in intensification of the kinetics of electrochemical reaction and thus explains the higher corrosion rate at elevated temperature. In 1.0 M HCl solution with 25 mM EABC concentration, the inhibition efficiency was found to be 72.55, 58.33 and 49.91 at 313, 323 and 333 K respectively (Figure 4).

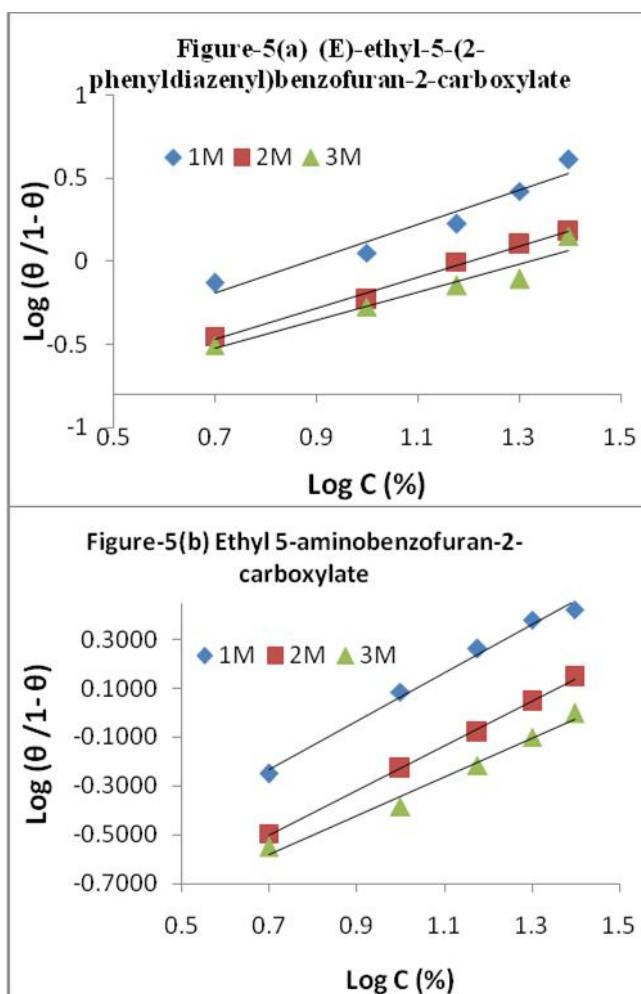
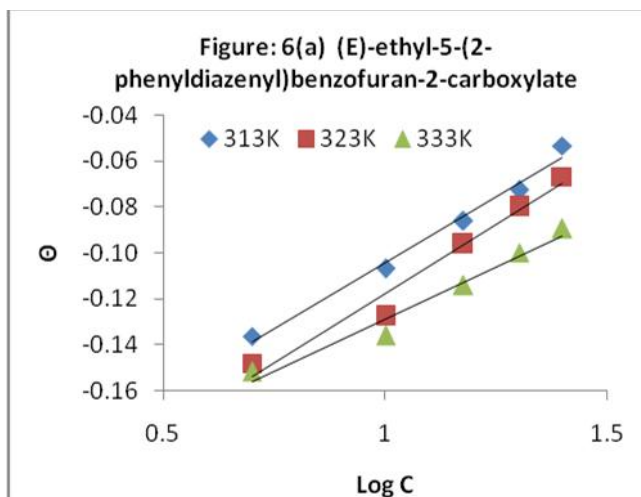


Figure 5(a) & 5(b): Plot of $\log (\theta / 1-\theta)$ versus $\log C$ for EPDBC & EABC respectively for 24h at 301 K.

In the present study general type of corrosion occurs predominately and less pitting. Plotting of $\log (\theta / 1-\theta)$ versus $\log C$ (%), straight lines were obtained, indicating that the adsorption of the added inhibitors followed the Langmuir adsorption isotherm (Figure 5a, 5b). Therefore, adsorption of these compounds is assumed to occur uniformly over the

metal surface. Plot a graph θ versus $\log C$ gives straight line (Figure 6a, 6b) showing that the adsorption of the compound on the mild steel surface from 1 M HCl obeys also Temkin's adsorption isotherm. It is also found that the degree of adsorption of the inhibitors increases with their concentration.



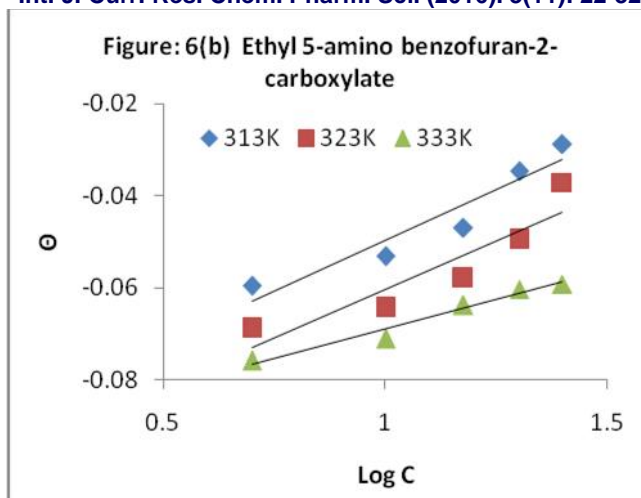


Figure 6(a)&6(b): Plot of θ versus $\log C$ for EPDBC & EABC respectively for 3h.

The values of the free energy of adsorption (G_{ads}^0) were calculated with the slope of the following equation .

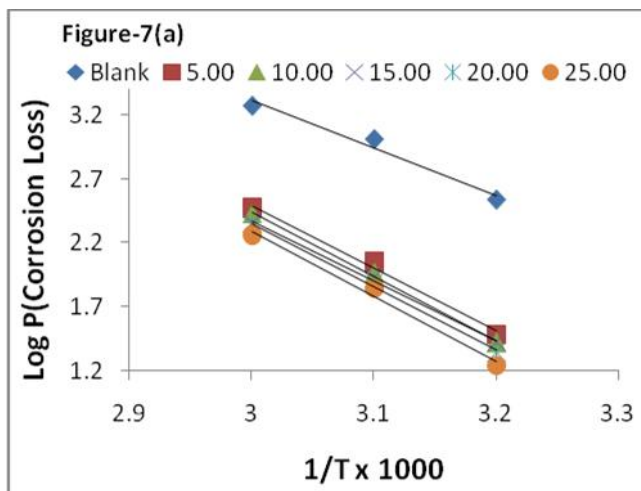
$$\text{Log} C = \text{Log} \left(\frac{n}{1-n} \right) - \text{Log} B \quad (4)$$

Where $\text{Log} B = -1.74 - \left(\frac{\Delta G_{ads}^0}{2.303RT} \right)$ and C is the inhibitor concentration. The mean G_a^0 values are negative almost in all cases and lie in the range of -3.78 to -8.92 kJ. mol⁻¹ shown in Table-1. The most efficient inhibitor shows more negative G_a^0 value. This suggests that they be strongly adsorbed on the metal surface.

The values of heat of adsorption (Q_{ads}) were calculated by the following equation.

$$Q_{ads} = 2.303R \left[\text{Log} \left(\frac{n_2}{1-n_2} \right) - \text{Log} \left(\frac{n_1}{1-n_1} \right) \right] \times \left[\left(\frac{T_1 T_2}{T_2 - T_1} \right) \right] \quad (5)$$

From Table -1, it is evident that in all cases, the (Q_{ads}) values are negative and ranging from -2.60 to -61.38 kJ. mol⁻¹. The negative values show that the adsorption, and hence the inhibition efficiency, decreases with a rise in temperature.



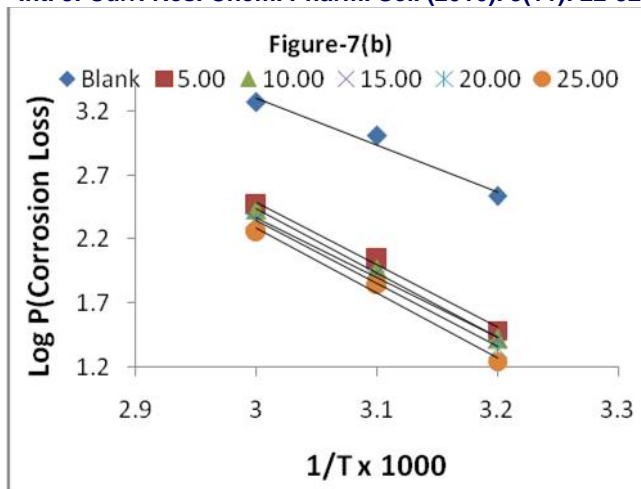


Figure 7(a) & 7(b): Arrhenius plots in absence and presence of EPDBC & EABC respectively.

Mean ' E_a ' value was calculated by using equation (6) for mild steel in 1M HCl is $72.79 \text{ kJ.mol}^{-1}$ while in acid containing inhibitor, the mean E_a values are found to be higher than that of an uninhibited system (Table 1). Higher values of E_a in the presence of the benzofurans which acts as inhibitor is a good indication of strong inhibiting action of the imidazoles by increasing the energy barrier for the corrosion process. Higher values of E_a in the presence of extract can also be correlated with the increase in thickness of the double layer that enhance the E_a of the corrosion process. The values of E_a calculated from the slope of an Arrhenius plot (Figure 7) and using equation (6) are almost similar. Energy of activation (E_a) has been calculated from the slopes of $\log p$ versus $1/T$ (p = corrosion rate, T = absolute temperature) and also with the help of Arrhenius equation.

$$\text{Log} \frac{P_2}{P_1} = \frac{E_a}{2.303R} \left[\left(\frac{1}{T_1} \right) - \left(\frac{1}{T_2} \right) \right] \quad (6)$$

Where p_1 and p_2 are the corrosion rate at temperature T_1 and T_2 respectively.

The enthalpy of adsorption (H_{ads}^0) and entropy of adsorption (S_{ads}^0) were calculated using the following equation (7) and (8).

$$\Delta H^0_{ads} = E_a - RT \quad (7)$$

$$\Delta S^0_{ads} = \frac{\Delta H^0_{ads} - \Delta G^0_{ads}}{T} \quad (8)$$

The enthalpy changes (H_a^0) are positive, indicating the endothermic nature of the reaction suggesting that higher temperature favors the corrosion process. The entropy (S_a^0) values are positive, confirming that the corrosion process is entropically favorable.

Table 1: Energy of activation (E_a), heat of adsorption (Q_{ads}) and free energy of adsorption (ΔG^0_{ads}) for mild steel in 1.0 M HCl Containing inhibitors.

System	Mean E_a from Eq.(6) (kJ. mol^{-1})	E_a from Arrhenius plot (kJ. mol^{-1})	Q_{ads} (kJ. mol^{-1})		Mean value (kJ. mol^{-1})		
			313-323 (K)	323-333 (K)	G^0_{ads}	H^0_{ads}	S^0_{ads}
Blank	72.79	70.38	-	-	-	-	-
EPDBC	93.65	90.32	-20.18	-28.86	-8.92	91.01	0.3095
EABC	93.57	90.18	-61.38	-33.03	-5.95	89.20	0.3065

Table 2: Polarization data and inhibition efficiency of EPDBC & EABC for mild Steel in 1 M HCl.

System	E_{corr} (mV)	i_{corr} (A/cm ²)	Tafel slope (V/decade)			Inhibition efficiency (%)	
			- c	+ a		Pol. Method From i_{corr}	Wt. loss method
Blank	-557	1.590×10^{-5}	5.75	1.44	2.64	-	-
EPDBC	-478	5.680×10^{-6}	216.1	100.8	158.33	99.88	80.39
EABC	-492	1.030×10^{-5}	125.4	84.3	116.1	93.79	72.55

Anodic and Cathodic polarization curves for mild steel in 1M HCl at 25mM inhibitor concentration of the presence and absence of inhibitors are shown in Figure 8 to 10. The value of the corrosion potential with inhibitors were found become more positive than the without inhibitors. Polarization study reveals that the inhibitors function as little anodic, but significant cathodic inhibitors, inhibitor functions as a mixed inhibitor. It is evident from the figure that cathodic tafel slopes (c) remain almost unchanged with increasing inhibitor concentration. This indicates that hydrogen evolution is activation controlled and the addition of inhibitor did not change the mechanism of cathodic

hydrogen evolution reaction ²³. The values for the Tafel parameters obtained from this plot with and without inhibitors are given in Table-2. The values of corrosion current densities in the presence and absence of inhibitor were obtained from the graph while percentage efficiency (%) was calculated using the Equation (8). The inhibition efficiency from Tafel plots agrees well (within ± 4 %) with the values obtained from weight loss data.

$$y(\%) = \left[\frac{i_{corr}(u) - i_{corr}(i)}{i_{corr}(u)} \right] \times 100 \quad (9)$$

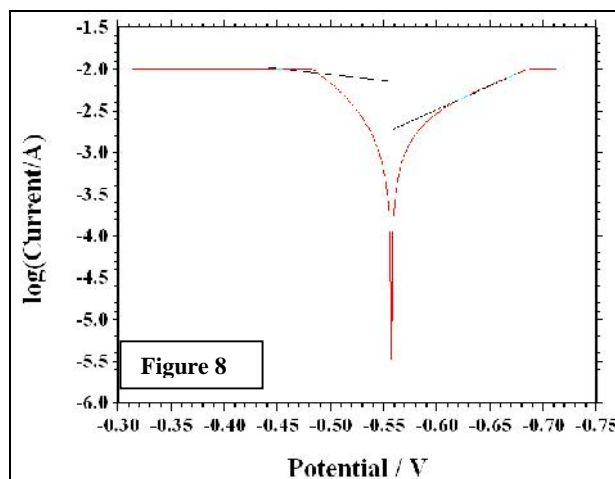


Figure 8: Polarisation curves for corrosion of mild steel in 1 M HCl.

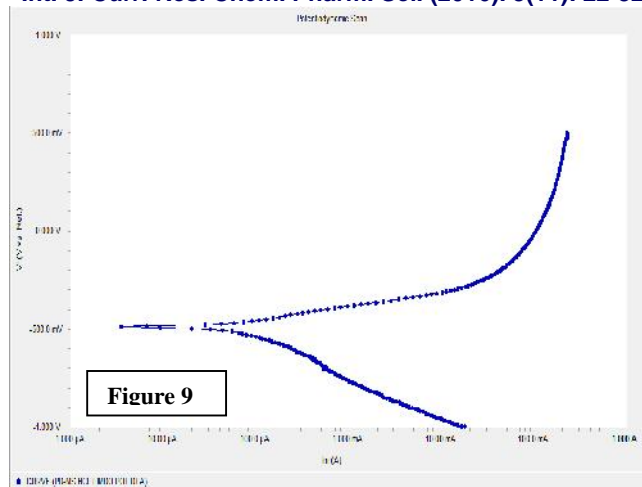


Figure 9: Polarisation curves for corrosion of mild steel in 1 M HCl containing 25 mm EPDBC.

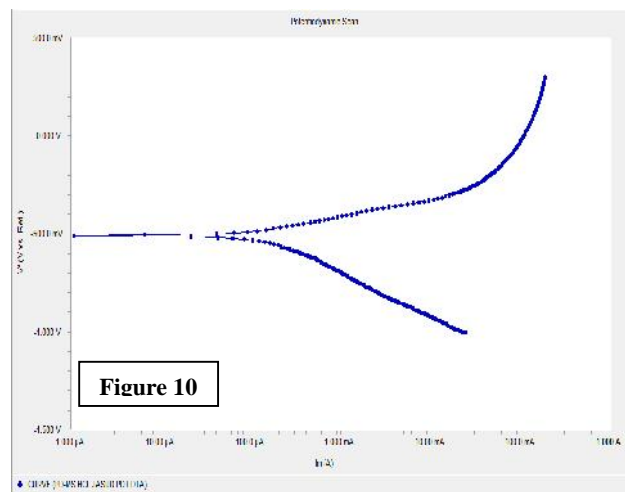
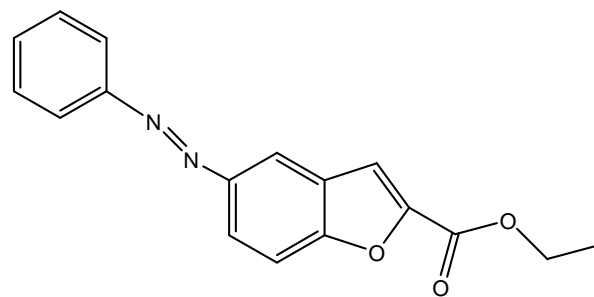
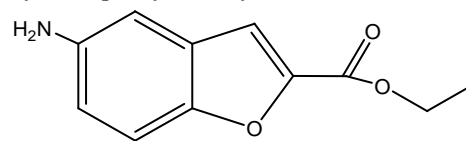


Figure 10: Polarisation curves for corrosion of mild steel in 1 M HCl containing 25 mm EABC

Mechanism:



(E)-ethyl 5-(2-phenyldiazenyl)benzofuran-2-carboxylate



ethyl 5-aminobenzofuran-2-carboxylate

The results of weight loss studies clearly demonstrate the superior performance of E-ethyl 5-(2-phenyl diazenyl) benzofuran-2-carboxylate (EPDBC) of benzofuran derivative containing organic group such as azo benzene than those containing amino (EABC). In the present investigation derivatives of benzofuran (EPDBC) exhibited the best performance due to presence of diazo group which is attached to the 5th carbon of benzofuran, aromatic ring and carboxylate anion.

According to another view, the molecules, attached through the polar atom or atoms, lie flat, so that each molecule covers up a considerable surface of element. Tests on heterocyclic compounds show that as the side chain is made longer, the efficiency increases. In the present investigation, it appears that the replacement of an amino group by diazo phenyl group improves the inhibitive action.

Conclusion

- As a constant inhibitor concentration, the inhibition efficiency of all inhibitors decreases as the concentration of acid increases.
- At all concentration of acid, as the inhibitor concentration increases inhibition efficiency increases and corrosion rate decreases.
- As the temperature increases corrosion rate increases in plain acid. Addition of inhibitors in corrosive media indicates that as the temperature increases corrosion rate increases while inhibition efficiency decreases.
- In all cases, the value of heat of adsorption (Q_{ads}) and the value of free energy of adsorption (G_a^0) is negative. The Value of change of enthalpy (H_a^0) and entropy of adsorption (S_a^0) is positive.
- A mean value of ' E_a ' in inhibiting acid is higher than the value of ' E_a ' in acid only.
- In almost all the cases, the inhibition efficiency from Tafel plots agrees well (within $\pm 19\%$) with the values obtained from weight loss data.

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