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## Evaluation of Some Synthesized Compounds as Corrosion Inhibitors in Oil Fields

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# Evaluation of Some Synthesized Compounds as Corrosion Inhibitors in Oil Fields

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## I. INTRODUCTION

Even with advanced corrosion resistant materials available, carbon steel has been widely employed as construction materials for pipe work in the oil and gas production such as down hole tubulars, flow lines and transmission pipelines [1]. Also, in oil fields hydrochloric acid solution is recommended as the cheapest way to dissolve calcium carbonate,  $\text{CaCO}_3$ , scale inside the pipelines under most conditions. Accordingly, corrosion inhibitors (usually surfactants) must be injected with the hydrochloric acid solution to avoid the destructive effect of acid on the surface of the pipe lines [2]. Corrosion inhibitors may be divided into three broad classes, namely oxidizing, precipitation and adsorption inhibitors.

Compounds containing nitrogen, oxygen, sulphur and phosphorus like hydroxy ethyl, amino ethyl and amido ethyl imidazoline in the conjugated system have particularly been reported as efficient corrosion inhibitors. These compounds can adsorb on the metal surface by blocking the active sites and thereby

decreasing the corrosion rate. The choice of inhibitors was based on the fact that these compounds contain  $\pi$ -electrons and heteroatom such as N, O and S which involve greater adsorption of the inhibitor molecules onto the surface of steel [3,4].

The aim of the present work is to study the inhibition of C-steel in 1 M HCl by some derivatives of phthalimide by two techniques (weight loss and electrochemical techniques). Weight loss measurements were used at different temperatures (303-333K) and the electrochemical technique is used at 303K.

## II. EXPERIMENTAL WORK

### a) Materials

#### i. Composition of material sample

The experiments were performed on samples of C-steel whose chemical composition (weight %) is as follows:  $C = 0.17\%$ ,  $Mn = 1.18\%$ ,  $P = 0.008\%$ ,  $Si = 0.27\%$ ,  $S = 0.008\%$ ,  $Cr = 0.27\%$ ,  $Mo = 0.04\%$ ,  $Fe = 98.05\%$ .

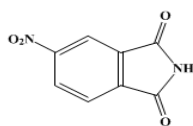
Specimens were mechanically polished with fine grade emery paper in order to obtain a smooth surface, followed by ultra sonically degreasing in acetone and then rinsed with distilled water, dried and weighed.

#### ii. Hydrochloric acid (BDH)

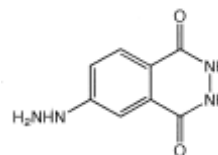
A stock solution of hydrochloric acid (8 M) was prepared using bidistilled water. The acid solution was prepared by diluting the appropriate volume of the concentrated chemically pure grade acid with bidistilled water. The concentration of the acid was checked by titration of an appropriately diluted portion with standard solution of analar sodium carbonate. 1 M HCl solutions were prepared by dilution using bidistilled water.

#### iii. Inhibitors

The organic inhibitors were prepared as before [5, 6 and 7].



4-nitrophthalimide  
(Compound A)



6-Hydrazinophthalazine-1, 4(2H,3H)-dione  
(Compound B)

#### iv. Inhibitor solutions

Five different concentrations viz, 50, 100, 150, 200 and 250 ppm from compounds A & B were used.

#### b) Methods

##### i. Weight loss method

Test pieces of C-steel (7 x 2 x 0.2 cm) were suspended by suitable glass hooks at the edge of the basin. The test specimen of C-steel was treated as described before and it had an average weight = 37.5 gm. It was dipped in 100 ml of test solution at 303K. This was conducted in a covered beaker to prevent contact with air and allow the escape of evolving gases. After the required immersion time, the test specimen was removed, washed with double distilled water, dried as before and finally weighed. The average weight loss at a certain time for the tested samples was taken in mg cm<sup>-2</sup>. The change in weight was recorded to the nearest 0.0001 g which is the sensitivity of the used analytical balance. Precautions were always made to avoid scratching the specimen during washing after exposure. Therefore, the weight losses/cm<sup>2</sup> are given from the equation:

$$\Delta W = (W_1 - W_2)/a \quad (1)$$

Where  $W_1$  and  $W_2$  are the weights of specimen before and after reaction, respectively and  $a$  is the surface area in cm<sup>2</sup>. The inhibition or acceleration efficiency  $\eta$  % was computed from the equation:

$$\theta = \frac{\Delta W - \Delta W_i}{\Delta W} \quad (2)$$

Where:  $\theta$  is the degree of surface coverage.

$$\eta \% = \frac{\Delta W - \Delta W_i}{\Delta W} \times 100 \quad (3)$$

Where,  $\Delta W$  and  $\Delta W_i$  are the weight loss per unit area in absence and presence of additive.

##### ii. Electrochemical method

Electrochemical measurements were carried out in a standard three-electrode cell. The counter electrode was a mesh of platinum of high purity (99.9%) and the reference electrode consisted of a saturated calomel electrode (SCE). The third electrode was the working electrode which was prepared from a round bar of carbon steel embedded in a cylindrical rod made out of Teflon. The cross-section area in contact with the solution was 1 cm<sup>2</sup>. All tests were performed in open air at room temperature of 303K. Electrochemical testing was performed using VOLTMASTER 4 version 4 through the galvanostatic polarization circuit at range from -1mV to 1mV for 20 min. The working electrode (WE) was polished mechanically. After polishing, the electrode was washed with acetone, rinsed several times with distilled water and dried. The freshly polished electrode was pretreated further before each experiment by holding the potential at -1 V vs. a saturated calomel electrode for 1min to reduce the oxide surface layer, and then open circuit potential ( $E_{ocp}$ ) was allowed to stabilize for 10 min.

### III. RESULTS AND DISCUSSION

#### a) Weight loss measurements

Weight loss in mg cm<sup>-2</sup> of the surface area for C-steel was determined in the absence and presence of the additives. Fig.1 shows the calculated weight loss/cm<sup>2</sup> for C-steel which was exposed to 1 M HCl at 303K in the absence and presence of 250 ppm from compounds A & B. The figure shows that weight loss for both compounds is lower than that for blank

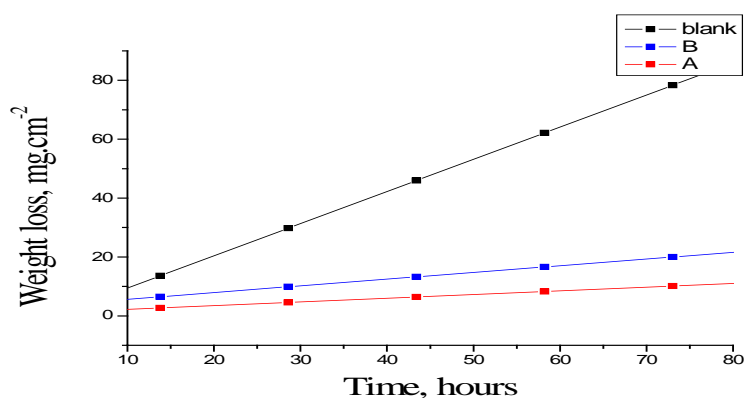


Figure 1: Weight loss-time curves for C-steel corrosion in the absence and presence of 250 ppm of A & B at 303K.

Rate of corrosion in mg.cm<sup>-2</sup> of the surface area for C-steel was determined in the absence and presence of the additives. It's obvious that the rate of corrosion of carbon steel in presence of inhibitors is much lower than that obtained in blank solution. Inspection of Table-1 reveals that, the inhibition

efficiency increase with an increase in inhibitor concentration. This behavior could be attributed to the increase of the number of adsorbed molecules at the metal surface. At one and the same inhibitors concentration the percentage of inhibition efficiency decreases in the following order: A > B. This increase

until 250 ppm after that there is no obvious increasing. Thus, at low concentrations (Sketch 1) a mono disordered layer may be formed while at high concentration, un-complete packing layer of the inhibitor molecules should be formed as shown in (Sketch 2). Meanwhile at maximum inhibition efficiency obtained,

the inter space area between the adsorbed inhibitor molecules on the surface may be lesser than the area of the inhibitor molecules. So that, the inhibitor molecules turn out to form the double layer adsorption as shown in (Sketch 3) [8].

**Table 1:** Corrosion Rate Dependence of Carbon Steel, the Degree of Surface Coverage ( $\theta$ ) at Different Concentrations of A and B in 1M HCl Solution at 303 K.

Concentration (ppm)	Rate of Corrosion (mg/cm <sup>2</sup> )		$\theta$		Efficiency $\eta$ (%)	
	A	B	A	B	A	B
Blank	8.48734	8.487339	/		/	
50	4.028088	4.073065	0.5254	0.5201	52.54	52.01
100	3.556181	3.836265	0.5810	0.5480	58.10	54.80
150	2.356929	3.254041	0.7223	0.6166	72.23	61.66
200	1.120319	2.580137	0.8680	0.6960	86.80	69.60
250	0.662851	2.534314	0.9219	0.7014	92.19	70.14



Sketch 1 : The adsorption of inhibitor on the surface at low concentration.



Sketch 2 : The adsorption of inhibitor on the surface at high concentration.



Sketch 3 : The adsorption of inhibitor on the surface at the maximum inhibition efficiency obtained (over dose concentration).

#### i. Effect of temperature

The effect of temperature on the rate of dissolution of carbon steel in 1M HCl containing 250 ppm of the inhibitors was studied by weight loss measurement over a temperature range from 303 to 333K.

Table-2 shows the effect of increasing temperature, as the temperature increases, the rate of

corrosion increases and hence the inhibition efficiency decreases. This is due to the adsorption is decreased by increasing the temperature. This behavior proves that the adsorption of inhibitors on C-steel surface occurs through physical adsorption.

**Table 2:** Corrosion Rate Dependence of Carbon Steel, the Degree of Surface Coverage ( $\theta$ ), the Percentage Inhibition ( $\eta$  %) in absence and presence of 250 ppm of A& B at Different Temperatures in 1M HCl Solution.

Temp. (K)	Corrosion Rate (k) (mg/cm <sup>2</sup> )			$\theta$		Efficiency $\eta$ (%)	
	Blank	A	B	A	B	A	B
303	8.4873	0.6628	2.5343	0.9219	0.7014	92.19	70.14
313	17.9303	2.6160	6.6216	0.8541	0.6307	85.41	63.07
323	42.4930	10.8867	17.2394	0.7438	0.5943	74.38	59.43
333	57.9389	16.7848	25.3714	0.7103	0.5621	71.03	56.21

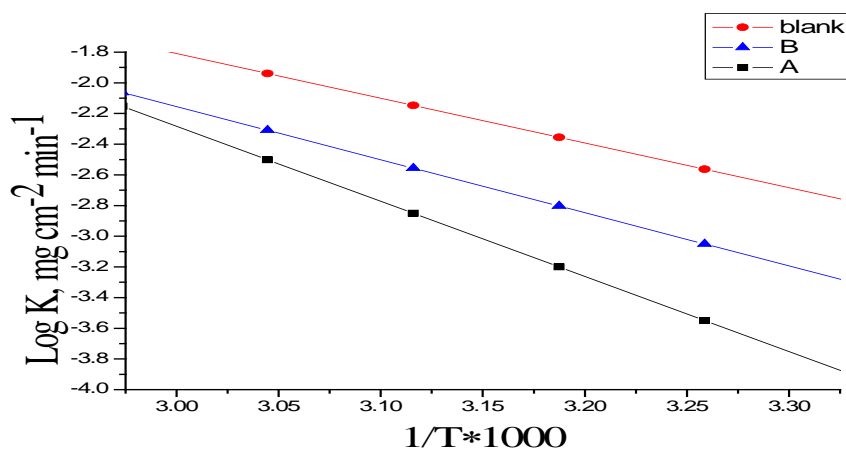


Figure 2 : a relation between Log K and 1/T for blank, A and B.

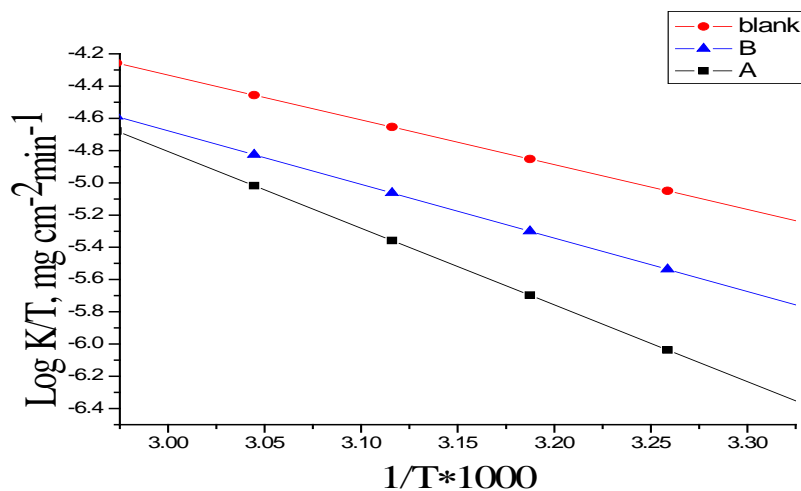


Figure 3 : a relation between Log K/T and 1/T for blank, A and B.

#### b) Activation parameters for dissolution

The apparent activation energy  $Ea^*$ , the enthalpy of activation  $\Delta H^*$ , the entropy of activation  $\Delta S^*$  and Gibbs free energy  $\Delta G^*$  for the corrosion of C-steel samples in 1 M HCl solutions in the absence and presence of different concentrations of inhibitors at 303–333K were calculated from Arrhenius equations:

$$K = A \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

$$K = \frac{RT}{Nh} \exp\left(\frac{\Delta S^\circ}{R}\right) \exp\left(\frac{-\Delta H^\circ}{RT}\right) \quad (5)$$

$$\Delta S^* = (\Delta H^* - \Delta G^*)/T \quad (6)$$

Where  $k$  is the corrosion rate,  $A$  is the frequency factor,  $h$  is the Plank constant,  $N$  is Avogadro's number and  $R$  is the universal gas constant. A plot of  $\log k$  vs.  $1/T$  and  $\log (k/T)$  vs.  $1/T$  give straight lines with slope of  $-Ea^*/2.303 R$  and  $-\Delta H^*/2.303 R$ , respectively. The

intercepts which are calculated will be  $A$  and  $\log R/Nh + \Delta S^*/2.303 R$  for Arrhenius and transition state equations, respectively.

Figs. 2-3 represent the plot of  $\log k$  vs.  $1/T$  and the plot of  $\log (k/T)$  vs.  $1/T$  data respectively in the absence and presence of 250 ppm of the investigated compounds. The calculated values of the apparent activation energy,  $Ea^*$ , activation entropies,  $\Delta S^*$  and activation enthalpies,  $\Delta H^*$  are given in Table 3. It is clear that the presence of tested compounds increased the activation values and consequently decreased the corrosion rate of C-steel. Also, the activation energy values increased by increasing the concentration of the inhibitors.

These results indicate that these tested compounds acted as inhibitors through increasing the activation energy of C-steel dissolution by making a barrier to mass and charge transfer by their adsorption on the C-steel surface. The values of  $\Delta H^*$  reflected the strong adsorption of these compounds on the C-steel surface. The values of  $\Delta S^*$  in the absence and presence of the tested compounds were negative; this indicates that the activated complex in the rate determining step

represents an association rather than dissociation step [9]. The values of  $\Delta G^*$  are all positive reflecting the high energy barrier for the corrosion process [10]. On the other hand,  $\Delta G^*$  values in presence of the inhibitors are higher than that obtained from 1M HCl (blank), and hence, the process is activation controlled. This means

that the activated molecules were in a higher order state than that at the initial state. The order of the inhibition efficiency of the investigated compounds as gathered from the increase in  $Ea^*$ ,  $\Delta H^*$  and the decrease in  $\Delta S^*$  values remains unchanged and follows the order  $A > B >$ .

Table 3: Thermodynamic Functions of Activation of the prepared inhibitors.

Inhibitor code	$\Delta E_a^*$ K.J.mol <sup>-1</sup>	$\Delta G^*$ K.J.mol <sup>-1</sup>	$\Delta H^*$ K.J.mol <sup>-1</sup>	$-\Delta S^*$ J.mol <sup>-1</sup> .K <sup>-1</sup>
Blank	55.83	77.80	58.42	60.95
A	93.81	149.09	96.38	165.76
B	66.33	96.19	68.91	85.81

c) adsorption isotherm

The Langmuir adsorption was calculated by.

$$C_i / \theta = 1 / K_{ad} + C_i \quad (7)$$

Where:  $C_i$  is the inhibitor concentration (in ppm).

$K_{ad}$  is the adsorption equilibrium constant.

Applying Langmuir adsorption equation (8) for the inhibitors, plots of  $C_i / \theta$  versus  $C_i$  are shown in Fig.4

Inspecting Langmuir plots for A and B, it is found that, all the investigated inhibitors showed linear plots. This behavior suggests that these inhibitors obey Langmuir adsorption. There is no interaction between the molecules adsorbed at the metal surface.

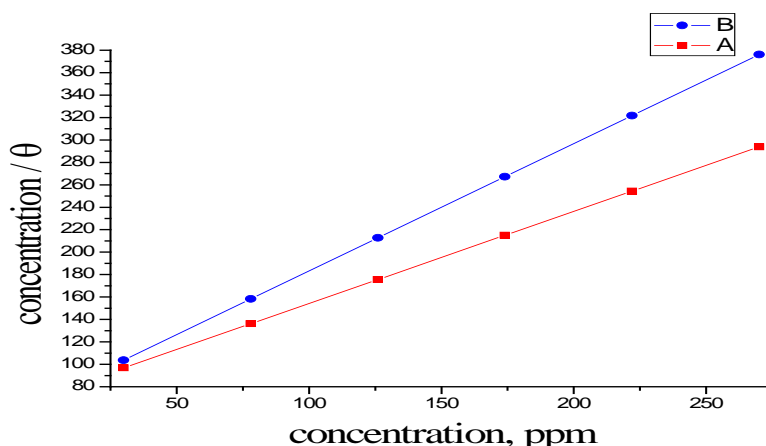
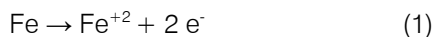


Figure 4: Langmuir adsorption isotherm for the inhibitor A & B on the carbon steel in 1M HCl at 298 K.

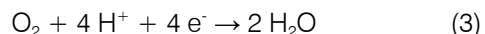
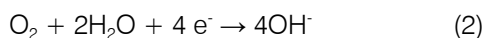
d) Potentiodynamic polarization measurements

i. Corrosion mechanism

A typical anodic oxidation that produces dissolved ionic products, for example for iron metal is:



Examples of cathodic reduction involved in corrosion process are:

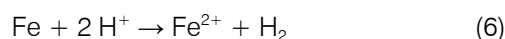


The cathodic reaction represented by equation (2) exemplifies corrosion in natural environments which

occurs at nearly neutral pH values. Equations (3) and (4) represent corrosion processes taking place in the acidic environments encountered in industrial processes where the pH can reach acidic values because of hydrolysis reactions such as:

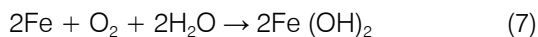


This reaction produces  $H^+$  ions, the concentration of which can, under certain conditions, become large if the  $H^+$  ions cannot readily move out from a confined volume. The overall corrosion reaction is, of course, For example,





Or, for a reaction producing hydroxide (sum of reactions 3 and 5):



ii. *Polarization measurements*

The efficiency was calculated from Potentiodynamic data according to equation 8 and 9.

$$\eta \% = 1 - (I_{\text{corr}} / I_{\text{corr}}^0) \quad 100 \quad (8)$$

$$\theta = (I_{\text{corr}}^0 - I_{\text{corr}}) / I_{\text{corr}}^0 \quad (9)$$

$$R_p = \frac{B}{I_{\text{corr}}} = \frac{(\Delta E)}{(\Delta I)} \quad (10)$$

Where  $I_{\text{corr}}$  is the current density in presence of inhibitors.

$I_{\text{corr}}^0$  is the current density in absence of inhibitors.

$\theta$ : Is the degree of surface coverage.

$R_p$ : Is the polarization resistance.

$B$ : Is constant =  $b_a \cdot b_c / 2.303 (b_a + b_c)$ .

$\Delta E$ : Is the potential difference.

$\Delta I$ : Is the current density difference.

The extrapolation of anodic and/or cathodic Tafel lines of charge transfer controlled corrosion reaction giving the corrosion current density,  $i_{\text{corr}}$ , at the corrosion potential,  $E_{\text{corr}}$ . This method is based on the electrochemical theory of corrosion processes developed by Wagner and Traud [11-14]. Anodic and cathodic polarization was carried out Potentiodynamically in unstirred 1 M HCl in the presence and absence of various concentrations of the compounds A&B at 303K. At all current densities, during

polarization, the overpotentials were slightly shifted with time and then attained steady values. These steady overpotentials values were used for the construction of anodic and cathodic Tafel plots. Figs.5-6 represent the Potentiodynamic polarization curves for the dissolution of C-steel in 1 M HCl in the presence and absence of different concentrations of the compounds at 303K. The numerical values of the variation of the corrosion current density ( $i_{\text{corr}}$ ), the corrosion potential ( $E_{\text{corr}}$ ), degree of surface coverage ( $\theta$ ) and the inhibition efficiency ( $I$  %) with the concentrations of different inhibitors are given in Tables 4-5. From the results in Figs. 5-6 and Tables 4-5 it was found that:

1. The cathodic and anodic curves which were obtained exhibited Tafel type behavior and the addition of the inhibitors increased both the cathodic and anodic overvoltages which caused mainly parallel displacement to the more negative and positive values respectively, i.e. the presence of inhibitors in solution inhibits both of hydrogen evolution and the anodic dissolution processes.
2. The corrosion current density ( $i_{\text{corr}}$ ) decreased with increasing the concentration of the inhibitors which indicated that these compounds acted as inhibitors, and the degree of inhibition depended on the concentration and type of the inhibitors present.
3. The values of polarization resistance of the inhibitors higher than the blank and its value increase with increasing the concentration of inhibitors.
4. The order of the inhibition efficiency of the inhibitors at different concentrations as given by polarization measurements is listed in Tables 4-5, where the arrangement of the compounds is ordered as in weight loss measurements as follows:  $A > B$

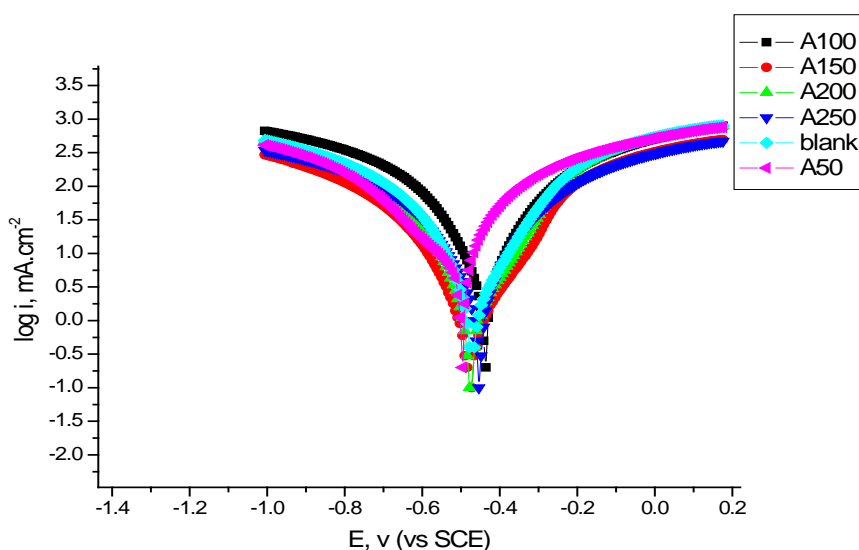


Figure 5 : Potentiodynamic polarization curves (E against log i) of carbon steel in 1M HCl in absence and presence of different concentrations of inhibitor A at 298 K.

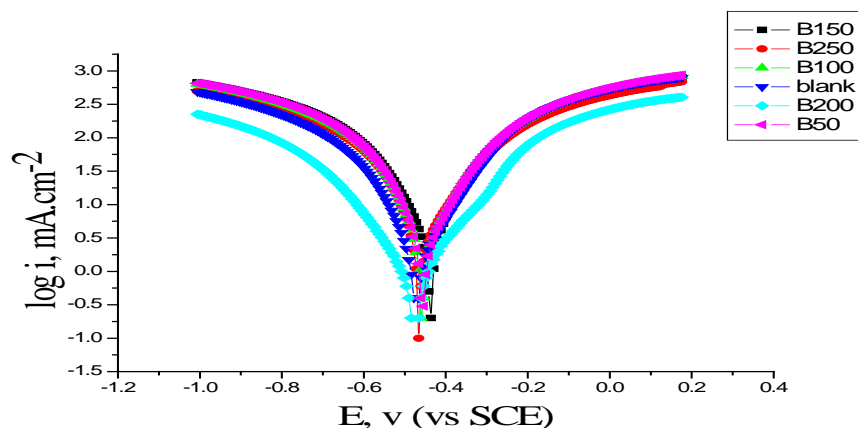


Figure 6 : Potentiodynamic polarization curves (E against log i) of carbon steel in 1M HCl in absence and presence of different concentrations of inhibitor A at 298 K.

Table 4 : Data from Potentiodynamic Polarization of Carbon Steel in 1 M HCl Containing Various Concentrations of Inhibitor A at 298 K.

Concentration, (ppm)	-E <sub>corr</sub> mV,	I <sub>corr.</sub> mA/cm <sup>2</sup>	R <sub>p</sub> , m(Ohm).cm <sup>-2</sup>	(θ)	η (%)
Blank	460	<b>0.39</b>	1.1	/	/
50	485	0.2	2.4	0.48	48.71
100	476	0.11	4.3	0.71	71.79
150	480	0.10	4.8	0.74	74.35
200	485	0.09	5.3	0.76	76.92
250	490	0.07	7.0	0.82	82.05

Table 5 : Data from Potentiodynamic Polarization of Carbon Steel in 1 M HCl Containing Various Concentrations of Inhibitor B at 298 K.

Coccentration, (ppm)	-E <sub>corr</sub> mV,	I <sub>corr.</sub> mA/cm <sup>2</sup>	R <sub>p</sub> , m(Ohm).cm <sup>-2</sup>	(θ)	η (%)
Blank	460	0.39	<b>1.1</b>	/	/
50	467	<b>0.28</b>	1.6	0.28	28.20
100	470	0.2	2.3	0.48	48.71
150	481	0.17	2.8	0.56	56.41
200	480	0.14	3.4	0.64	64.10
250	485	0.09	5.3	0.76	76.92

#### IV. CONCLUSION

1. The inhibition efficiency of the studied inhibitors increases in the following order: 4-nitrophthalimide > 6-Hydrazinophthalazine-1,4(2H,3H)-dione
2. The inhibition efficiency of all studied inhibitors increases with increasing the concentration.
3. The maximum recommended dose is 250 ppm.
4. The values of activation energy (E<sub>a</sub><sup>\*</sup>) increases in the same order of increasing the inhibition efficiency of the inhibitor.

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