

# Structural investigation of pyrazole derivatives as corrosion inhibitors for delta steel in acid chloride solutions

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The effect of type and position of the substituted group of pyrazole derivatives for corrosion inhibition of Delta steel in acid chloride solutions has been investigated. It was found that increase of inhibitor concentration decreased both the corrosion rate,  $R_{\text{corr}}$ , and the corrosion current,  $i_{\text{corr}}$ , and shifted the corrosion potential,  $E_{\text{corr}}$ , to more positive values, i.e. the predominant action was as an anodic inhibitor. The results showed that the adsorption isotherm is S-shaped. The inhibition efficiency of the different substituted pyrazole derivatives follows the order: methyl < methoxyl < chloro. On the other hand, the position of the substituent group with respect to the azo group of the pyrazole derivatives, affected the inhibition efficiency as follows: ortho < para < meta. Also, the effect of temperature on the corrosion inhibition was found to follow an Arrhenius relation.

## 1. Introduction

Various organic compounds have been used as corrosion inhibitors for mild steel in different acid media [1-7]. The inhibition efficiency of the compounds was related to the polar group and the size of the N-substituted group [4]. The effect of electronic delocalization in the alkyl group of thiocarbonyl, R-CS-NH<sub>2</sub>, and related compounds on inhibition efficiency of iron in 1.0 M HCl solutions was studied by Donnelly *et al.* [8]. The inhibition efficiency of the compound was found to be related qualitatively to the electronic resonance in the R group. Frignani *et al.* [9] improved the inhibition efficiency of N-decylpyridinium derivatives by the introduction of suitable substituents in the 3-position of the aromatic ring. These derivatives act mainly by physical adsorption between the organic cation and the anions, Cl<sup>-</sup> or Br<sup>-</sup>, pre-adsorbed at the metal surface of the electrode. The organic cations mainly inhibit the H<sup>+</sup> ion discharge, but, when present in higher concentrations, they also inhibit the iron dissolution reaction.

The distribution of the  $\pi$ -electron density on the reaction centres of the inhibitor molecules was compared with the electrochemical characteristics of the corrosion process and the adsorption properties of the molecules [10, 11]. The protective effect of the inhibitors is caused by the chemisorption of molecules on the metal surface and depends substantially on the polar properties of the molecules. Majda [12] studied the corrosion inhibition of nitrogen-containing compounds in aqueous acid chloride solutions at high temperatures for preventing corrosion of steel pipes. Evaluation of corrosion inhibition in concentrated HCl solutions at high temperatures was investigated by Hausler [13].

In previous work, the parent inhibitor used, 4-arylazopyrazolo-3,5-diamine, was found to inhibit the corrosion of Delta steel in acid chloride media [14]. So, the aim of this work is to demonstrate the correlation between the type and position of the substituent, with respect to the pyrazole ring, and the corrosion inhibition for Delta steel in acid chloride solutions. The effect of temperature is also studied.

## 2. Experimental details

The steel used was Delta 37-carbon steel produced by Delta Steel Mill Company, Egypt. It had the following composition (in percentages):

C	Si	S	Mn	P	Ni	V	Ti	Al
0.08	0.05	0.005	0.02	0.015	0.016	0.03	0.008	0.04

The preparation of the electrodes and the specimens for weight loss and polarization measurements, the electrolytic cell and the electric circuit for polarization measurements have been described elsewhere [15, 16]. All solutions were prepared from AnalaR chemicals and triply distilled water. The electrode potential was measured against a saturated calomel electrode (SCE). The polarization experiments were started after the attainment of stable values for the corrosion potentials. For weight loss measurements, a steel sheet of surface area *c.* 16 cm<sup>2</sup>, after polishing with 2/0 emery papers, degreased and dried by a jet air, was dipped in 50 ml of the test solution for definite time intervals. The inhibition efficiency was calculated from the following equations:

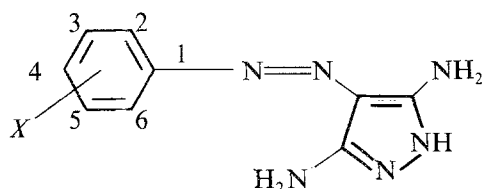
$$I\% = \frac{\Delta W^0 - \Delta W_{\text{inh}}}{\Delta W^0} \times 100 \quad (1)$$

and

$$I\% = \frac{i_0 - i_{inh}}{i_0} \times 100 \quad (2)$$

where  $\Delta W^0$  and  $\Delta W_{inh}$  are the weight loss per unit area and  $i_0$  and  $i_{inh}$  are the corrosion current densities in the absence and presence of additive, respectively.

The organic additives used as inhibitors were selected from the pyrazole series. They were prepared and crystallized several times according to Elgemeie *et al.* [17]. The substances were 4-aryloxy-3,5-diamine (parent), *p*, (*x*-chloroaryloxy)pyrazolo-3,5-diamine (CIP), (*x*-methoxy-aryloxy)pyrazolo-3,5-diamine (MeOP) and (*x*-methylaryloxy) pyrazolo-3,5-diamine (MeP) in which *x* represents the position of the substituent in the 4 (para), 3 (meta) and 2 (ortho) positions, respectively. The structures are as follows:



where  $x = -H(P)$ ,  $-Cl(CIP)$ ,  $-OCH_3(MeOP)$  or  $-CH_3(MeP)$ .

### 3. Results and discussion

#### 3.1. Effect of type and position of substituted group

The three substituted groups studied were methyl, methoxyl, as electron-donating, and chloro, as electron-withdrawing group, located in the para, meta, or ortho position of the phenyl ring with respect to the azopyrazole derivative. The inhibition of such derivatives were compared with those of the parent pyrazole compound (P) using weight loss and galvanostatic polarization measurements. Figures 1a to c show the variation of corrosion potential,  $E_{corr}$ , with the logarithm of inhibitor concentration in 0.5 M acid chloride solutions. From the figure it is seen that  $E_{corr}$  shifts to less negative values with increasing inhibitor concentration for each derivative, that is, they act predominantly as anodic inhibitors. On the other hand, for each concentration, the unsubstituted pyrazole derivative, P, shows more negative  $E_{corr}$  while MeOP and CIP give less negative values.

The effect of the substitution group and its position on the inhibition efficiency of the parent pyrazole derivative (P) can be evaluated from the amount of potential shift,  $\Delta E_{shift}$ , that is,  $E_{parent} - E_{substituted}$  at constant concentration (see Table 1). As can be seen from Figs 2 and 3, the amount of potential shift, to less negative values, increases with an increase of inhibitor concentration. On the other hand, for the same inhibitor concentration the lowering of potential to less negative value with substituted group increases in the following order:

methyl < methoxyl < chloro

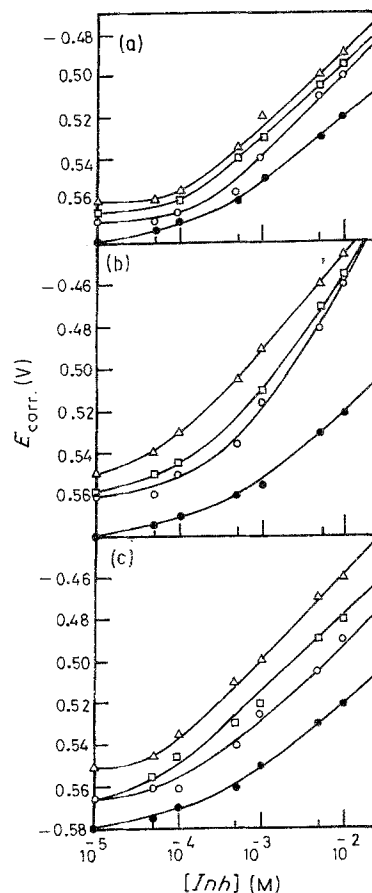


Fig. 1. Variation of corrosion potential,  $E_{corr}$ , with logarithm of inhibitor concentration for Delta steel in 0.5 M acid chloride solutions. (a) Ortho substituted derivatives, (b) meta substituted and (c) para substituted.  $\circ$  - methyl,  $\square$  - methoxyl,  $\Delta$  - chloro derivatives and  $\bullet$  - parent pyrazole compound.

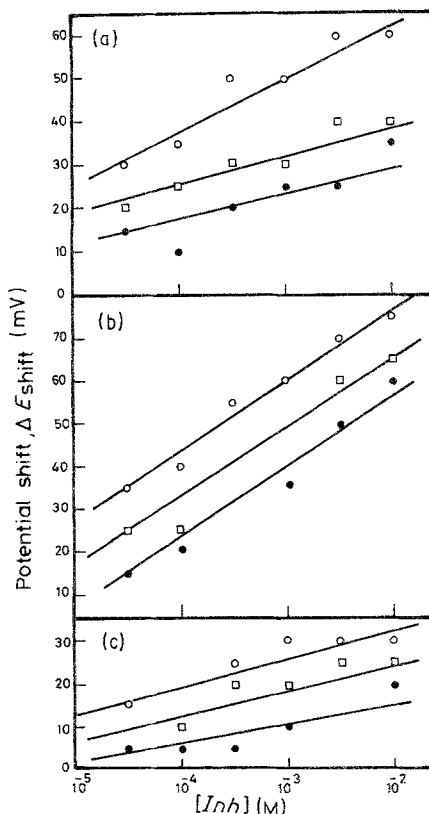


Fig. 2. Variation of potential shift,  $\Delta E_{shift}$ , with  $[Inh]$  for Delta steel in 0.5 M acid chloride solutions. (a) Para substituted, (b) meta substituted and (c) ortho substituted.  $\bullet$  - methyl,  $\square$  - methoxyl and  $\circ$  - chloro derivatives.

Table 1. The potential shift,  $\Delta E_{\text{shift}}$  (mV), for the different substituted groups located in various position with respect to unsubstituted derivatives

$E_{\text{shift}}$ (mV) [Inh] (M)	CH <sub>3</sub> -			H <sub>3</sub> CO-			Cl-		
	o-	m-	p-	o-	m-	p-	o-	m-	p-
$5 \times 10^{-5}$	5	15	10	15	25	20	14	35	30
$1 \times 10^{-4}$	6	20	12	17	26	25	15	40	35
$5 \times 10^{-4}$	7	25	18	20	30	30	25	55	47
$1 \times 10^{-3}$	10	35	23	22	40	32	29	60	50
$5 \times 10^{-3}$	20	50	26	25	60	40	30	70	60
$1 \times 10^{-2}$	22	60	30	26	65	42	32	75	62

and for a given substituent, the efficiency of inhibition varies with its position according to the following order:

$$\text{ortho} < \text{para} < \text{meta}$$

From the results of weight loss and polarization measurements, the surface coverages were obtained using the following equations:

$$\theta = \frac{\Delta W^0 - \Delta W_{\text{inh}}}{\Delta W^0} \quad (3)$$

and

$$\theta_i = \frac{i_0 - i_{\text{inh}}}{i_0} \quad (4)$$

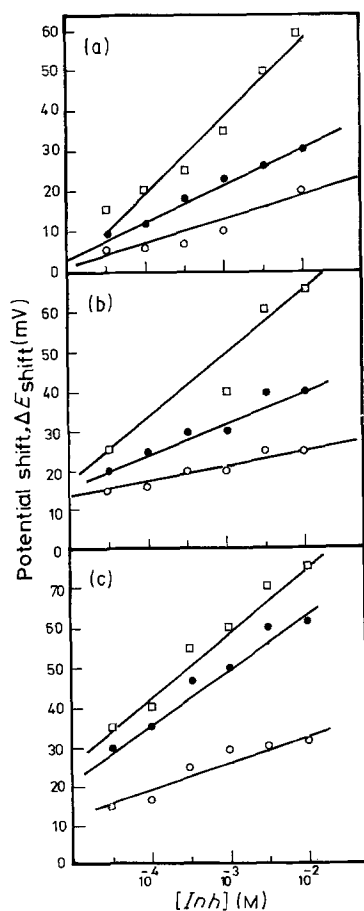


Fig. 3. Variation of potential shift,  $\Delta E_{\text{shift}}$ , with [Inh] for Delta steel in 0.5 M acid chloride solutions. (a) Methyl derivative, (b) methoxyl and (c) chloro.  $\circ$  — ortho,  $\bullet$  — para and  $\square$  — meta positions with respect to azo group of pyrazole compound.

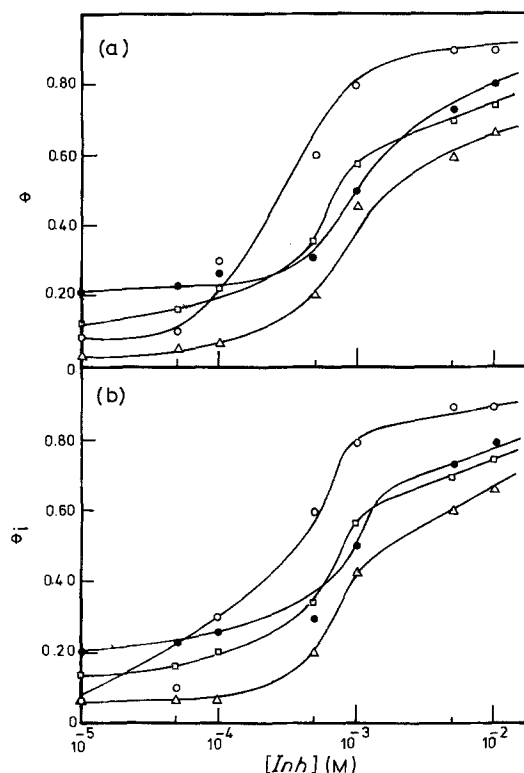


Fig. 4. Variation of surface coverage,  $\theta$  and  $\theta_i$  with logarithm of [Inh] for p-derivatives, calculated from: (a) weight loss and (b) polarization measurements.  $\Delta$  — parent,  $\square$  — p-CH<sub>3</sub>,  $\bullet$  — p-CH<sub>3</sub>O and  $\circ$  — p-Cl.

where  $\Delta W^0$ ,  $i_0$ ,  $\Delta W_{\text{inh}}$  and  $i_{\text{inh}}$  are the weight loss and corrosion current density in the absence and presence of inhibitor, respectively. Figures 4 and 5 show the variation of  $\theta$  and  $\theta_i$  with the logarithm of inhibitor

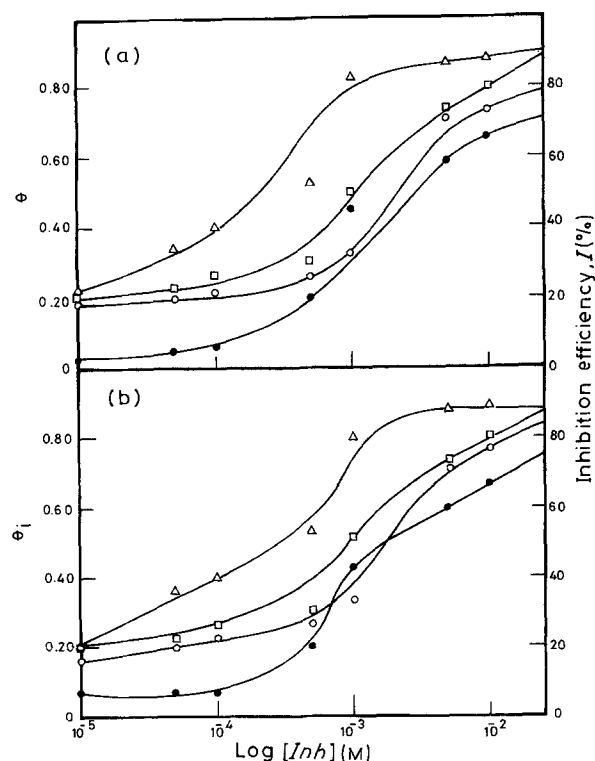


Fig. 5. Variation of surface coverage,  $\theta$  and  $\theta_i$ , and inhibition percentage,  $I$  (%), with the log of the inhibitor concentration calculated from (a) weight loss and (b) polarization measurements.  $\Delta$  — CH<sub>3</sub>-,  $\square$  — CH<sub>3</sub>O- and  $\bullet$  — Cl- derivatives.



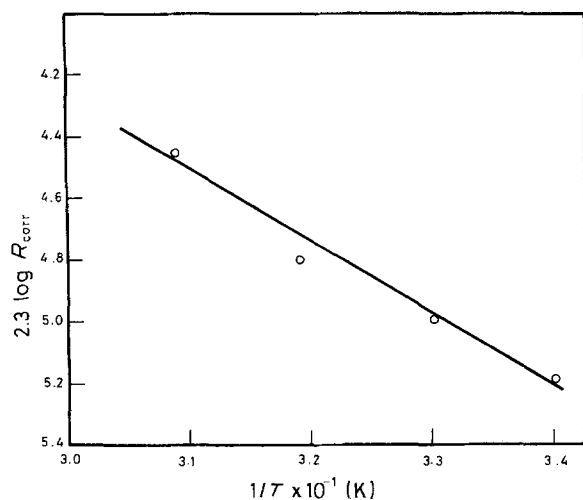


Fig. 8. Arrhenius plot of  $\log R_{\text{corr}}$  against  $1/T$  for Delta steel in 0.5 M HCl solutions.

Fig. 8. The variation is linear and obeys the following equation:

$$2.303 \log R_{\text{corr}} = \beta - \frac{\Delta E_a}{R} \frac{1}{T} \quad (7)$$

where  $\beta$  is a constant depending on the metal type and electrolyte, respectively. The activation energy,  $\Delta E_a$ , calculated from the slope ( $2.303 \log R_{\text{corr}}/d(1/T)$ ) is equal to  $19.1 \text{ kJ mol}^{-1}$ . Ateya *et al.* [23] found that the activation energy of  $51.4 \text{ kJ mol}^{-1}$  for iron in 5 N  $\text{H}_2\text{SO}_4$  solution was identical to that reported by Hudson *et al.* [24], and by Selim *et al.* [25]. Also, Maitra and Singh [26] found that the activation energy for low carbon steel in 1 N  $\text{H}_2\text{SO}_4$  solution was  $4.81 \text{ kJ mol}^{-1}$ . Generally, one can say that the nature and concentration of the electrolyte greatly affect the activation energy for the corrosion process.

On the other hand, the variation of inhibition efficiency of the pyrazole compound (P) with temperature was followed using weight loss and polarization measurements. Table 3 shows that  $E_{\text{corr}}$  drifts to a less negative potential with an increase in temperature. The amount of potential shift  $\Delta E_{\text{shift}}$ , with respect to  $E_{\text{corr}}$  at  $20^\circ\text{C}$ , increases linearly with  $1/T$ , see Fig. 9. Also, the variation of the logarithm of the surface coverage,  $\theta$  and  $\theta_i$ , with  $1/T$  (in Fig. 10), is linear with slopes  $0.16 \times 10^4$  and  $0.15 \times 10^4$ , respectively. Accordingly, the activation energies calculated from weight loss and polarization measurements are 13.3 and

Table 3. Variation of  $E_{\text{corr}}$ ,  $i_{\text{corr}}$ ,  $R_{\text{corr}}$  and surface coverage,  $\theta$  and  $\theta_i$ , for Delta Steel in 0.5 M acid chloride solutions containing pyrazole compound,  $[P] = 10^{-3} \text{ M}$ , with temperature

Temperature ( $^\circ\text{C}$ )	$E_{\text{corr}}$ (V)	$i_{\text{corr}}$ ( $\text{A cm}^{-2} \times 10^{-4}$ )	$R_{\text{corr}}$ ( $\text{g cm}^{-2} \text{ s}^{-1}$ )	Surface coverages	
				$\theta$	$\theta_i$
20	-0.580	6.5	0.002998	0.466	0.500
30	-0.570	6.0	0.003140	0.522	0.571
40	-0.560	5.2	0.002910	0.651	0.665
50	-0.550	4.0	0.003500	0.738	0.750

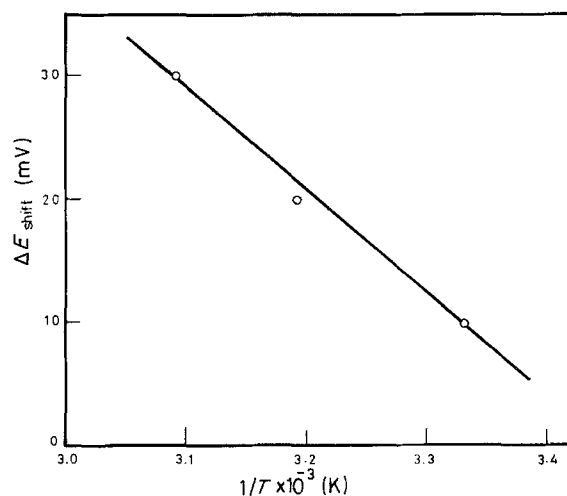


Fig. 9. Dependence of potential shift,  $\Delta E_{\text{shift}}$ , with the reciprocal of absolute temperature,  $1/T$ , for Delta steel in 0.5 M acid chloride solutions containing pyrazole compound,  $[P] = 10^{-3} \text{ M}$ .

$12.5 \text{ kJ mol}^{-1}$ , respectively. Such results indicate that the presence of inhibitor causes a significant change in the value of the apparent activation energy. Also, the obtained value,  $\approx 12.9 \text{ kJ mol}^{-1}$ , for the  $10^{-3} \text{ M}$  pyrazole compound in 0.5 M HCl solution is comparable with that for a diffusion controlled process [27]. This suggests that pyrazole brings about a change in the rate determining step from the hydrogen evolution reaction (r.d.s. in absence of inhibitor) to a slow diffusional step. It is well known that anodic metal dissolution reactions are often inhibited by the presence of protective films on the metal surface. The diffusion of metal ions through these films then becomes rate determining.

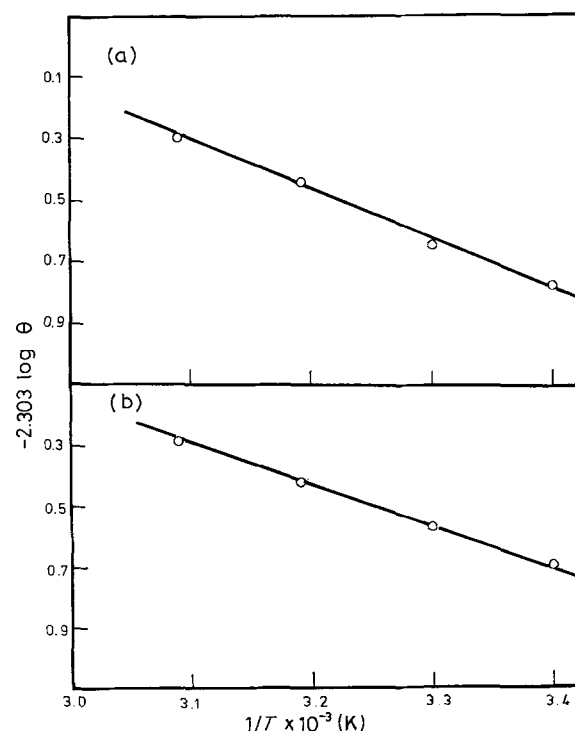


Fig. 10. Arrhenius plot of  $\log \theta$  and  $\theta_i$ , with  $1/T$  for Delta steel in 0.5 M acid chloride solutions containing pyrazole compound,  $[P] = 10^{-3} \text{ M}$ , calculated from (a) weight loss and (b) polarization measurements.

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