

2,5-Disubstituted 1,3,4-Oxadiazole Derivatives as Effective Inhibitors for the Corrosion of Mild Steel In 2M H₃PO₄ Solution

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The influence of three oxadiazole derivatives on the corrosion inhibition of steel in 2M H₃PO₄ solution is studied using weight-loss and electrochemical polarisation measurements. The results show that 2,5-bis(4-methoxyphenyl)-1,3,4-oxadiazole (P4) is the best inhibitor and its inhibition efficiency increases with the increase of concentration to attain 76% at 5×10^{-4} M. Potentiodynamic polarisation studies clearly reveal that the oxadiazole derivatives act essentially as cathodic inhibitors. The inhibition efficiency of the studied oxadiazoles decreases with the rise in temperature in the range 298-348 K. E% values obtained from weight-loss and electrochemical methods were in good agreement. Adsorption of P4 on steel surface has an S-shaped adsorption isotherm.

Keywords: 1,3,4-Oxadiazole derivatives; Mild steel, Phosphoric acid; Corrosion Inhibition; Adsorption process

1. INTRODUCTION

The search for new and efficient corrosion inhibitors becomes an obligation to secure metallic materials against corrosion. The effectiveness of organic compounds containing heteroatoms as corrosion inhibitors for steels in sulphuric acid is well developed [1-7]. The adsorption of inhibitors

takes place through heteroatoms such as nitrogen, oxygen, phosphorus and sulphur, triple bonds or aromatic rings. Studies show that inhibition efficiency of organic compounds may be explained on the basis of structural molecules. The nature of heteroatom and substituents plays the major role in adsorption phenomenon. Also the existing data show that most organic inhibitors adsorb on the metal surface by displacing water molecules on the surface and forming a compact barrier film [8].

Recently many workers have reoriented their attention to the development of new corrosion inhibitors based on organic compounds as pyrazole [9-14], triazole [15-20], tetrazole [21-25], imidazole [26-28], oxadiazole derivatives [29-32], containing nitrogen, oxygen, sulphur atoms, and multiple bonds in the molecules that facilitate adsorption on the metal surface. The corrosion inhibition efficiency of organic compounds is related to their adsorption properties. Studies report that the adsorption of organic inhibitors mainly depends on some physicochemical properties of the molecule, related to its functional groups, to the possible steric effects and electronic density of donor atoms. Adsorption is supposed also to depend on the possible interaction of π -orbitals of the inhibitor with d -orbitals of the surface atoms, which induces greater adsorption of the inhibitor molecules onto the surface of carbon steel, leading to the formation of a corrosion protecting film.

Many workers have determined thermodynamic parameters such as adsorption heat, adsorption entropy and adsorption free energy are obtained from experimental data of the temperature studies of the inhibition process at different temperatures. The kinetic data such as apparent activation energy and pre-exponential factor at different concentrations of the inhibitor are calculated, and the effects of the activation energy and pre-exponential factor on the corrosion rate of steel are discussed [33-37]. The inhibition action is satisfactorily explained by using both thermodynamic and kinetic models.

Our earlier results obtained for 2,5-bis (n-methoxyphenyl)-1,3,4-oxadiazoles as corrosion inhibitors of mild-steel demonstrated that correlation exists between inhibition efficiency and chemical structure [37]. It was found that these compounds are good inhibitors in acidic solutions and the inhibition efficiency of these oxadiazole-type organic compounds may be explained in terms of electronic properties [the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), band gap $\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}}$, and the dipole moment (μ)]. In this work, the influence of three oxadiazole derivatives on the corrosion inhibition of steel in 2M H_3PO_4 solution is studied using weight-loss and electrochemical polarisation measurements. Also, the aim of this paper was to extend these investigations in order to obtain a better understanding of the mode of inhibitory action of 2,5-bis(4-methoxyphenyl)-1,3,4-oxadiazole (P4) by calculating thermodynamic parameters for both mild steel dissolution and inhibitor adsorption process in phosphoric acid solution using weight loss measurements.

2. EXPERIMENTAL DETAILS

Corrosion tests were performed on a mild steel of the following percentage composition: 0.21 % C; 0.38 % Si; 0.09 % P; 0.01 % Al; 0.05 % Mn; 0.05 % S and the remainder iron. For the gravimetric measurements, pre-treatment of the surface of specimens was carried out by grinding with emery paper of 600–1200 grit, rinsing with bidistilled water, ultrasonic degreasing in ethanol, and dried at room temperature before use. The aggressive solutions 2M H_3PO_4 , were prepared by dilution

of an analytical reagent grade 85 % H_3PO_4 with bidistilled water. The tested inhibitors, namely (P1, P3 and P4) were synthesised according to a previously described experimental procedure [38]. The molecular structures of inhibitors are shown in Fig. 1.

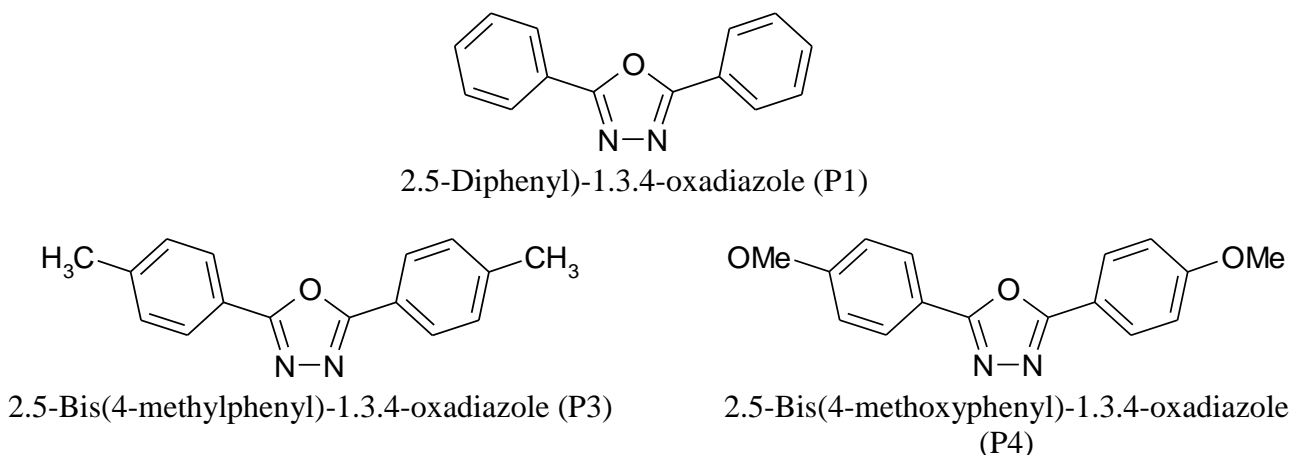


Figure 1. Molecular structures of the studied oxadiazole derivatives.

Gravimetric experiments were carried out in a double glass cell equipped with a thermostated cooling condenser. The solution volume was 60 ml. The used steel specimens had a rectangular form (length = 2 cm, width = 2 cm, thickness = 0.05 cm). At the end of the tests the specimens were carefully washed in ethanol under ultrasound, and then weighed. Duplicate experiments were performed in each case and the mean value of the weight loss has been reported. Weight loss allowed us to calculate the mean corrosion rate as expressed in $\text{mg cm}^{-2} \text{h}^{-1}$.

3. RESULTS AND DISCUSSION

3.1. Comparative study

The effect of addition of tested oxadiazole compounds at 10^{-3}M on the corrosion of steel in 2M H_3PO_4 is studied by weight-loss at 298 K after 2 hours of immersion period. Table 1 collects the corresponding values of corrosion rates of steel and inhibition efficiency.

Examination of efficiency of tested inhibitors may be explained on the basis of their structural molecules. The substitution of hydrogen in P1 (63.3%) by methyl group leads to a decrease of inhibition P3 (54.3%), but with methoxy $-\text{OCH}_3$ which acceptor inductive and mesomery donor increases the adsorption to attain 69.3%. P4 shows a good inhibition (69.4%). An intramolecular effect between oxadiazole ring and two phenyl rings supported by methoxy group.

The inhibition efficiency of oxadiazole compounds follows the sequence:

$$\text{P3 (54.3\%)} < \text{P1 (63.3\%)} < \text{P4 (69.4\%)}$$

Table 1. Corrosion rate of mild steel and inhibition efficiency for various concentrations of 1,3,4-oxadiazole derivatives in the corrosion of mild steel in 2 M H₃PO₄l obtained from weight loss measurements

Inhibitor	Concentration (M)	W (mg cm ⁻² h ⁻¹)	E (%)
Blank	—	1.410	—
P1			
	1×10 ⁻⁶	1.388	1.5
	5×10 ⁻⁵	1.240	11.8
	1×10 ⁻⁵	1.151	18.3
	5×10 ⁻⁵	0.816	42.1
	1×10 ⁻⁴	0.697	50.6
	5×10 ⁻⁴	0.517	63.3
P3			
	1×10 ⁻⁶	1.42	0
	5×10 ⁻⁵	1.330	6.
	1×10 ⁻⁵	1.220	13.5
	5×10 ⁻⁵	0.970	31.
	1×10 ⁻⁴	0.810	43.
	5×10 ⁻⁴	0.644	54.3
P4			
	1×10 ⁻⁶	1.250	11.3
	5×10 ⁻⁵	1.064	24.5
	1×10 ⁻⁵	0.712	49.5
	5×10 ⁻⁵	0.536	62.0
	1×10 ⁻⁴	0.476	66.2
	5×10 ⁻⁴	0.431	69.4

Polarisation curves of steel electrode in 2M H₃PO₄ at different concentrations of P1 and P4 and at 5.10⁻⁴ M P3 were collected in Fig. 2. Corresponding electrochemical parameters and related inhibition efficiencies (E%) were given in Table 2.

The addition of the three oxadiazoles leads to a decrease in the cathodic current densities. The cathodic portions rise to Tafel lines indicating that the hydrogen evolution reaction is activation controlled. The addition of the inhibitor to the corrosive solution does not modify the cathodic Tafel slope b_c and then the mechanism of the reduction process is not affected. The free corrosion potential determined after 30mn of immersion does not change in the presence of the inhibitor. This phenomenon is more pronounced with the concentration of inhibitor. E% values increase with the concentration of inhibitor and attains a maximum value of 75.6 % at 5.10⁻⁴ M of P4. In anodic domain the curve characteristics are slightly modified in the presence of inhibitor. The polarisation curves for steel in 2M H₃PO₄ show that the presence of oxadiazoles inhibits only cathodic process and then they act essentially as cathodic inhibitors.

Table 2. Electrochemical parameters of mild steel in 2M H₃PO₄ at various concentrations of oxadiazole derivatives.

	Concentration (M)	E_{corr} (mV)	b_c (mV/dec)	I_{corr} (mA.cm ⁻²)	E (%)
Blank	—	-465	198	0.533	—
P1	5×10^{-4}	-482	178	0.213	60.0
	1×10^{-4}	-472	184	0.270	49.3
	5×10^{-5}	-475	176	0.311	41.6
	1×10^{-5}	-488	178	0.396	25.7
	5×10^{-6}	-476	193	0.443	16.9
	1×10^{-6}	-474	192	0.515	3.4
P3	$5 \cdot 10^{-4}$	-478	177	0.227	57.4
P4	5×10^{-4}	-480	158	0.130	75.6
	1×10^{-4}	-486	162	0.173	67.5
	5×10^{-5}	-482	161	0.179	66.4
	1×10^{-5}	-477	171	0.231	56.7
	5×10^{-6}	-470	188	0.405	24.0
	1×10^{-6}	-472	184	0.450	15.6

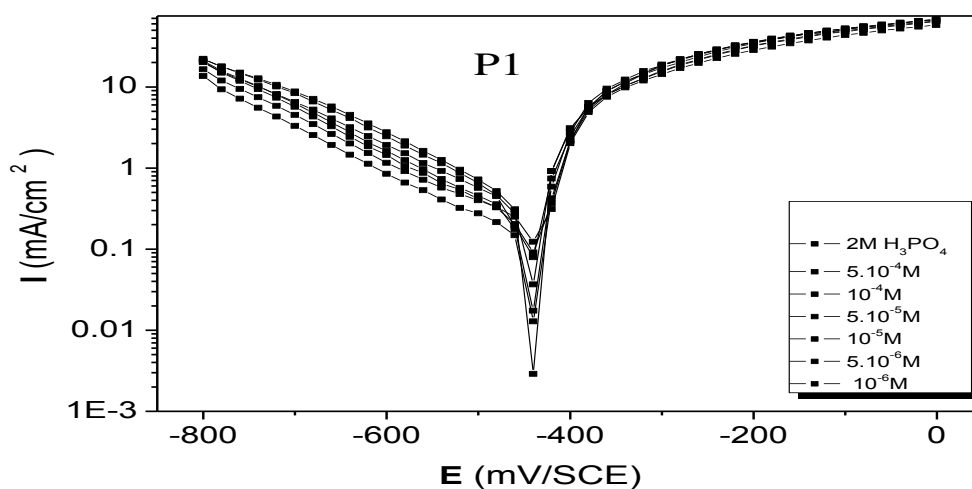


Figure 3a. Polarisation curves of steel in 2M H₃PO₄ with and without P1 at different contents.

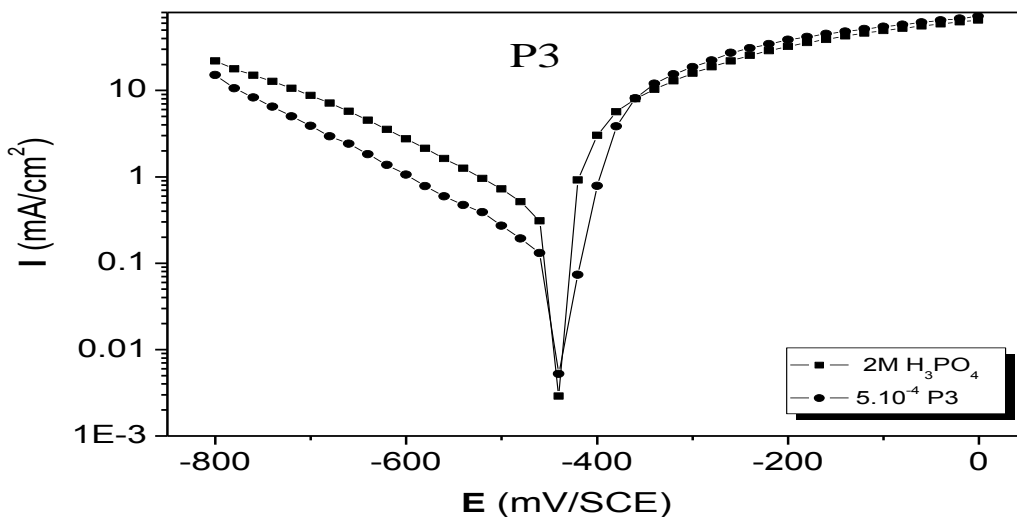


Figure 3b. Polarisation curves of steel in 2M H₃PO₄ with and without P3 at 5×10⁻⁴M.

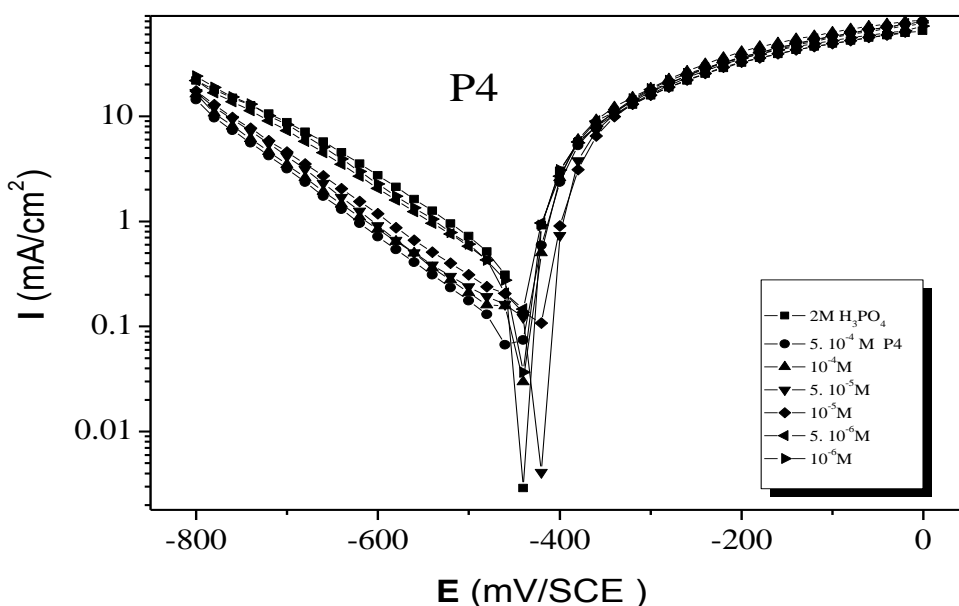


Figure 3c. Polarisation curves of steel in 2M H₃PO₄ with and without P4 at different contents.

3.2. Effect of temperature

The corrosion rate of mild steel in acidic solution increases with the temperature. Popova et al. interpreted this phenomenon by the decrease of hydrogen evolution overpotential [39]. Increased temperature gives reduced viscosity ν and increased diffusion coefficient D , and the total effect of temperature on the boundary layer thickness δ is therefore relatively small [40]. The performance of the oxadiazole tested with the activation processes may be investigated by studying the effect of temperature. For this purpose, the weight loss measurements in 2M H₃PO₄ in the absence and presence of 5×10⁻⁴M 2,5-bis(4-methoxyphenyl)-1,3,4-oxadiazole (P4) are being employed with the range of temperature 298, 308, 318, 328, 338 and 348K for 1h of immersion (Table 3). The corrosion reaction is usually regarded as an Arrhenius process and the rate (W) is expressed by the relation:

$$\log(W) = \frac{-E_a}{RT} + A$$

where E_a is the activation energy of the corrosion process.

Table 3. Effect of temperature on the corrosion of steel with and without 5×10^{-4} M of Oxadiazole derivatives.

T (K)	W_0 (mg/cm ² h)	W (P4) (mg/cm ² h)	E (P4) (%)	W (P1) (mg/cm ² h)	E (P1) (%)	W (P3) (mg/cm ² h)	E (P3) (%)
298	1.41	0.431	69.43	0.517	63.33	0.6439	54.33
308	2.6	0.874	66.38	1.012	61.05	1.58	46.11
318	5.514	1.986	63.98	2.591	53.01	3.883	30.75
328	9.83	4.489	54.33	5.38	45.26	9.225	10.61
338	17.87	10.688	40.19	13.06	26.91	17.169	6.46
348	25.11	16.12	35.80	20.44	18.59	25	0.0

From these results, we can deduce that the corrosion rate increases in the blank with the rise of temperature, but in the presence of oxadiazoles, the dissolution of steel is retarded but according to the nature of substituent of the molecule. At higher temperature, P3 shows zero efficiency, but P4 resists for moderate temperature to decrease thereafter. For the corrosion rate of steel were given in. Table 4 gathered the calculated values of activation energies in the presence and absence of oxadiazoles issued from Arrhenius plots (Fig. 4). Activation energy in the presence of inhibitors, $E_a(P4) = 65.2$, $E_a(P3) = 65.2$, $E_a(P1) = 66.1$ kJ mol⁻¹ were higher than that in uninhibited acid, $E_a = 51.3$ kJ mol⁻¹. The higher value of the activation energy of the process in an inhibitor's presence when compared to that in its absence is attributed to physical adsorption [39].

Table 4. Effect of temperature on the corrosion of steel with and without 5×10^{-4} M of oxadiazole derivatives.

	Pre-exponential factor (mg/cm ² h)	Linear regression coefficient (r)	E_a (kJ/mol)
Blank	1.3902×10^9	0.997	51.3
P4	1.0771×10^{11}	0.997	65.2
P1	1.8287×10^{11}	0.997	66.1
P3	1.8381×10^{11}	0.995	65.2

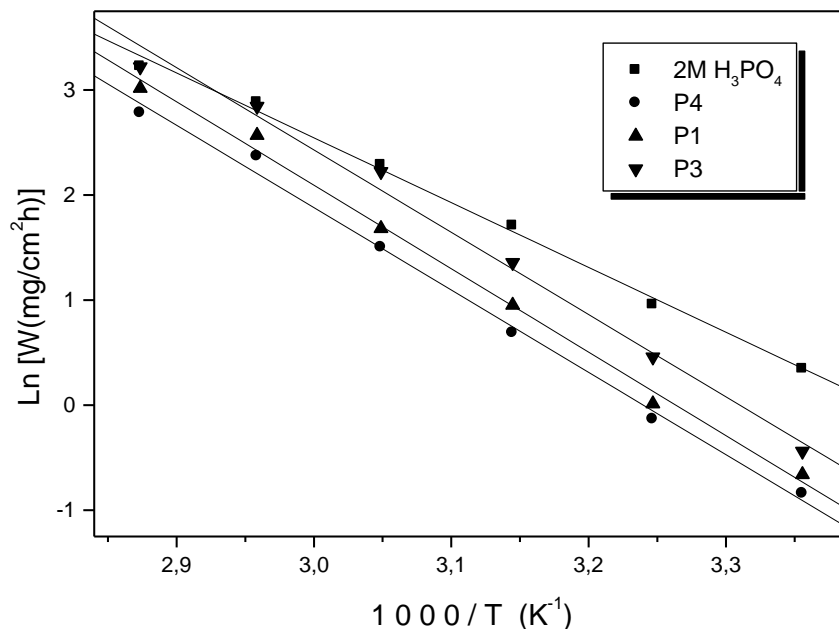


Figure 4. Arrhenius plots for steel in 2M H₃PO₄ with and without at 5×10⁻⁴M of P1, P3 and P4.

3.3. Electrochemical impedance spectroscopy measurements

The corrosion behaviour of steel, in acidic solution in the presence of P4 at different concentrations was investigated by EIS measurements at room temperature and shown in Fig. 5. The locus of Nyquist plots is regarded as one part of a semicircle. The charge transfer resistance, R_{ct}, the double layer capacitance C_{dl}, the frequency f_{max} values were given in Table 5.

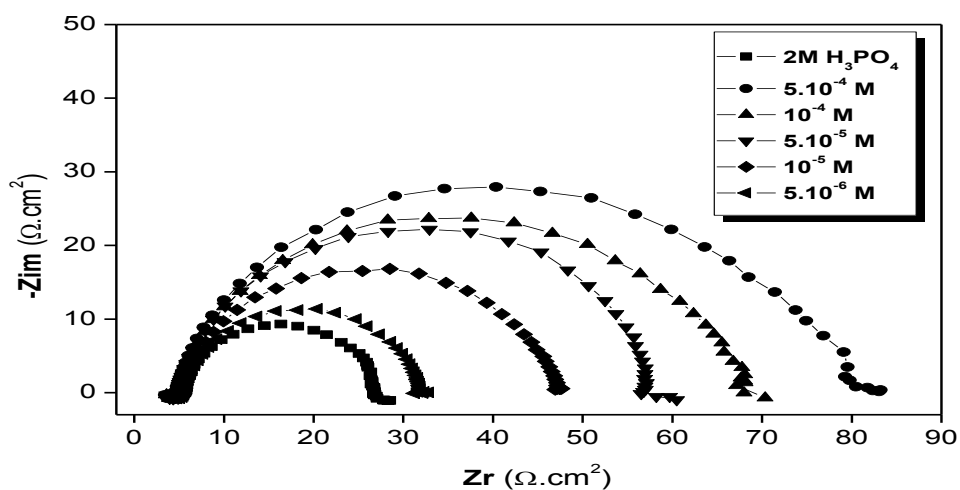


Figure 5. Nyquist diagrams for mild steel in 2M H₃PO₄ with different concentrations of P4.

Table 5. Ac impedance data for mild steel in 2M H₃PO₄ in presence and absence of P4.

	Concentration (M)	R _{ct} (Ω.cm ²)	f _{max} (Hz)	C _{d1} (μF/cm ²)	E (%)
blank	—	20.8	89.28	85.7	×
	5×10 ⁻⁴	71.68	50	44.4	71
	1×10 ⁻⁴	63.39	44.64	56.2	67
P4	5×10 ⁻⁵	52.97	56.18	53.5	61
	1×10 ⁻⁵	41.8	50	76.1	50
	5×10 ⁻⁶	26.35	71.42	84.6	21

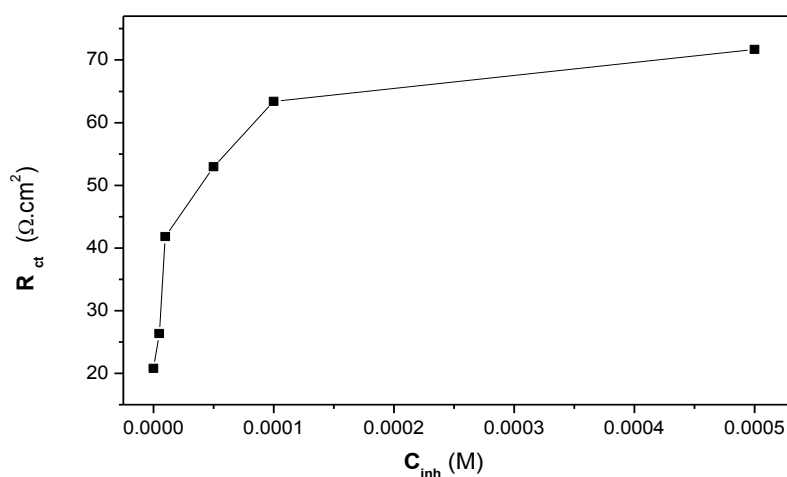


Figure 6. Evolution of R_{ct} with the concentration of P4.

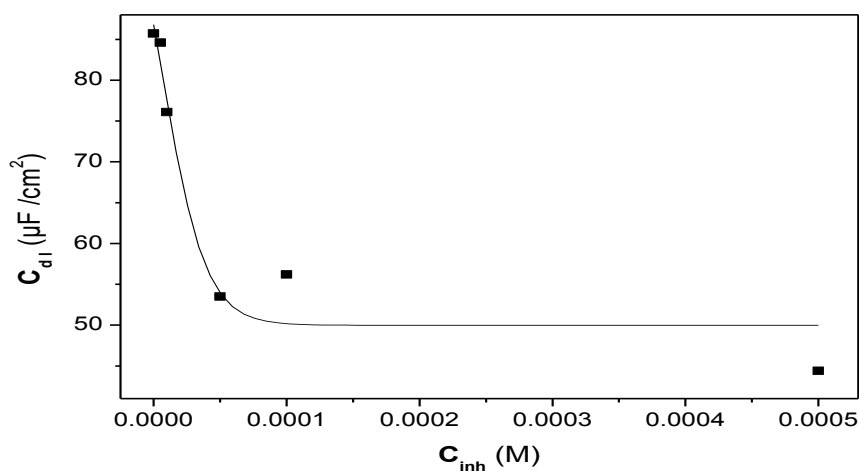


Figure 7. Evolution of C_{d1} with the concentration of P4.

The obtaining of the semicircle in the impedance diagrams indicated that the corrosion of steel is controlled by a charge transfer process. Table 5 shows the impedance parameters obtained by line fitting to the semicircle. The charge transfer resistance (R_{ct}) increases with the inhibitor concentration (Fig. 6). Also, the double layer capacitance (C_{dl}) decreases with increase in the concentration of the inhibitor (Fig. 7). This decrease is due to adsorption of inhibition the metal surface causing a change of the double layer structure [41]. When comparing the inhibition efficiencies obtained from testing methods used in this study, it can be concluded that there is a fair agreement between results obtained by the different techniques used.

3.4. Adsorption isotherm

Fig. 8 illustrates the dependence of the fraction of the surface covered (C_{inh}/θ) as function of the concentration of the Oxadiazole. θ is the ration $E(\%) / 100$. The linear plot shows a Langmuir adsorption isotherm for Oxadiazole compound represented by the following equation:

$$\frac{C_{inh}}{\theta} = \frac{1}{K} + C_{inh}$$

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G^{\circ}_{ads}}{RT}\right)$$

C_{inh} is the inhibitor concentration, K_{ads} the equilibrium constant of the adsorption reaction and ΔG°_{ads} the standard free energy of adsorption.

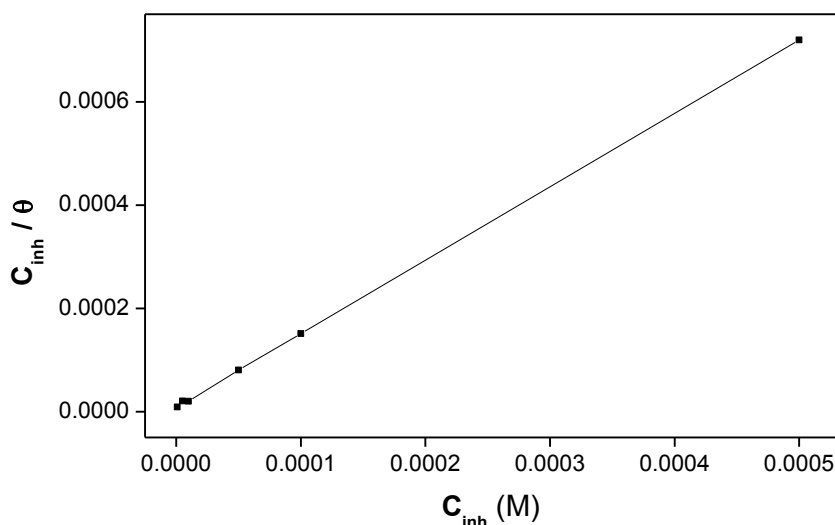


Figure 8. Isotherm adsorption model of P4 on the steel surface in 2M H_3PO_4 .

$K_{ads} = 110193 \text{ M}^{-1}$, $\Delta G^{\circ}_{ads} = -38.75 \text{ kJ mol}^{-1}$, Slope = 1.4 and $R = 0.999$. The negative value of ΔG°_{ads} suggests that the tested molecules of P4 were spontaneously adsorbed on the metal surface.

Khamis et al. pointed out when value of $\Delta G^{\circ}_{\text{ads}}$ is more negative than -40 kJ mol^{-1} , chemisorption takes place by charge sharing or transfer from the organic molecule to the metal surface to form a coordinate type of bond [42]. Values of activation energy that is around -20 to -40 kJ mol^{-1} can be suggested to obey the physical adsorption (physisorption) mechanism. Physisorption is often related with this phenomenon, where an adsorptive film of electrostatic character is formed on the mild steel surface. In addition, high value of activation energy will lower the corrosion rate or lower the corrosion current density. The obtained value ($-38.75 \text{ kJ mol}^{-1}$) indicates that the adsorption mechanism of P4 on mild steel surface in $2\text{M H}_3\text{PO}_4$ probably involves two types of interactions, predominant physisorption (ionic) and weak chemisorption (molecular).

5. CONCLUSION

The main conclusions drawn from this study are:

- The inhibition efficiency of oxadiazole compounds may be classified as: $\text{P3} < \text{P1} < \text{P4}$.
- P4 is an efficient inhibitor for steel in $2\text{M H}_3\text{PO}_4$
- The inhibition efficiency of P4 attains a maximum value of 69.4% at $5 \times 10^{-4} \text{ M}$.
- It acts as a cathodic inhibitor without modifying the mechanism of hydrogen evolution.
- The inhibition efficiency of P4 decreases with temperature.
- P4 adsorbs according to the Langmuir adsorption isotherm

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