EIS Evaluation of Pantoprazole as Corrosion Inhibitor for Mild Steel Immersed In HCl 1 M. Effect of [Pantoprazole], Hydrodynamic Conditions, Temperature and Immersion Times

A. Espinoza-Vázquez^{1,2}, G.E. Negrón-Silva¹, D. Angeles-Beltrán¹, H. Herrera-Hernández³, M. Romero-Romo², M. Palomar-Pardavé^{2,*}

¹ Universidad Autónoma Metropolitana-Azcapotzalco, Departamento de Ciencias Básicas, Av. San Pablo No. 180, México D.F., C.P. 02200, México.

² Universidad Autónoma Metropolitana-Azcapotzalco, Departamento Materiales, Av. San Pablo No. 180, México D.F., C.P. 02200, México.

³ Universidad Autónoma del Estado de México, C.U. Valle de México, Ingeniería Industrial. Blvd. Universitario s/n, Predio San Javier Atizapán de Zaragoza 54500, México. *E-mail: mepp@correo.azc.uam.mx

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The corrosion behavior of pipeline steel grade API 5L X52 immersed in a 1M HCl aqueous solution in the presence and absence of Pantoprazole, was evaluated using EIS. The effect of different experimental conditions namely: Pantoprazole concentration, electrode rotation speed, temperature and immersion times on the corrosion inhibition efficiency (IE) of Pantoprazole, were evaluated. It is shown that at stagnant conditions (0 rpm) the IE increased with inhibitor concentration, reaching a value of ca. 93% at 25 ppm, which remains constant up to 200 ppm. When the steel working electrode rotation speed was varied, it was found that for [Pantoprazole] \geq 25 ppm, the IE reached a maximum value, ca. 95%, at 40 rpm, however, it diminished to ca. 85% when the electrode rotation speed reached 1000 rpm. Furthermore, when the temperature of the corrosive media was increased from 25 to 60 °C, at stagnant conditions with 25 ppm Pantoprazole, the IE values diminished to ca. 60%. For stagnant conditions, 50 ppm Pantoprazole and 25 °C, an IE greater that 93% was found for the inhibitor even after 700 exposure hours to the corrosive media. Lastly, the results showed that, in all cases, the Pantoprazole inhibition mechanism involves blockage of the steel surface throughout a Langmuir-type physisorption process.

Keywords: Pantoprazole; pipeline steel; HCl; corrosion inhibition; EIS; hydrodynamic conditions; temperature

1. INTRODUCTION

Mild steel is widely applied in industrial manufacturing, particularly in the automotive and machinery segments, due to its low production costs coupled to excellent mechanical properties and overall integral reliability, however the steel displays a clear tendency to corrode in diverse environmental conditions. Today, various preventive methods are available at fairly low costs to reduce the corrosion rate of such alloys in acidic environments. Among them, significant improvements have been made available regarding the corrosion resistance properties of mild steel, particularly in corrosive aqueous media through addition of corrosion inhibitors [1-23]. The list of molecules that have proven to be effective as corrosion inhibitors for mild steel immersed in different sorts of corrosive media is rather large [24]. However, just a few studies in this respect have been reported using the so called green corrosion inhibitors [25], which are biodegradable and do not contain heavy metals or other toxic compounds. For instance, Pantoprazole, see Figure 1, can be considered as a green corrosion inhibitor; primarily it is a medicament inhibitor of the stomach's proton pump used for the short term treatment of erosions and ulcers caused by gastro esophageal reflux disease [26-29]. This compound contains many π electrons and heteroatoms like nitrogen, sulfur, four oxygen atoms and two fluorines, all of which are thought to be capable of inducing better adsorption of the molecule, compared with other heterocyclic compounds [30]. It is relevant to point out that the compound comprises the basic structure of 2-mercaptobenzimidazole in its oxidized form, which our research group has previously shown to be efficient when added up to 25 ppm reaching a 96% IE in H_2SO_4 [1]. Furthermore, Pantoprazole has been reported by our group [31] and more recently by Quraishi [32] to have inhibitory corrosion properties for mild steel immersed in 1.0 M HCl, attaining 97.78 % IE at an optimum concentration of 60 ppm under stagnant conditions.



Figure 1. Molecular structure of Pantoprazole: (*RS*)-6-(Difluoromethoxy)-2-[(3,4-dimethoxypyridin-2-yl)methylsulfinyl]-1*H*-benzo[*d*]imidazole.

Consequently, our interest in evaluating this organic molecule containing other substituents such as OCH₃ but particularly fluorine atoms, stems from the fact that the molecule displays also biological inhibitory activity [33], thus making it a bifunctional material equally proper for engineering uses under different hydrodynamic conditions and temperatures.

2. EXPERIMENTAL METHODOLOGY

From a 0.01 M Peucetol (Pantoprazole) solution containing the active ingredient 5-(difluoromethoxy)-2-(((3,4-dimethoxypiridin-2-yl)methyl)sulfinyl)-1Hbenzoimidazole in an ethanolwater mixture 50/50, Pantoprazole aliquots (5-200 ppm) were prepared in 50 ml 1M HCl.

The electrochemical study was conducted in a typical three-electrode electrochemical cell, using a saturated Ag/AgCl reference electrode, a graphite rod as counter electrode, and rotating disk electrode of the API 5L X52 steel sample as the working electrode. The latter was prepared from rectangular API 5L X52 pipeline steel coupons, which after their electrical connection by means of a copper wire, were encapsulated in an epoxy resin at room temperature, so as to expose approximately 1 cm² surface area to the corrosive electrolyte. Prior to each experiment, the electrodes' surface were prepared using conventional metallographic methods. Subsequent to cleaning the electrodes were ultrasonicated with ethanol for 10 min and rinsed with acetone: after, they were finally dried in warm air. The electrolyte was 1 M HCl (blank) and each of the Pantoprazole aliquots mentioned above, then the working electrode was immersed in the test solution prepared during 15 min until a steady-state open circuit potential (Eocp) was measured. Electrochemical impedance measurements, EIS, were performed using the Zahner Zennium electrochemical workstation, with a small sinusoidal perturbation signal of ± 10 mV around E_{corr}, within the 10⁶ to 10⁻² Hz frequency range, recording 10 points per decade. The experimental impedance data obtained for different inhibitor's concentration, namely: 0, 5 - 200 ppm, with the hydrodynamic conditions: 0, 40, 100 and 1000 rpm and temperatures: 25, 40 and 60 °C. The EIS results were represented using Nyquist plots. The chargetransfer resistance, R_{ct} and the double-layer capacitance (C_{dl}) values, were calculated by fitting an appropriate equivalent electrical circuit (EEC) to the experimental data points of the impedance plots. Moreover, the effect of exposure time of the steel sample to the corrosion media was also evaluated

3. RESULTS AND DISCUSSION

3.1 Influence of the inhibitor concentration and electrode rotation speed

The experimental impedance plot of the steel immersed in HCl, without Pantoprazole (namely the blank) is shown in Figure 1a. From this plot it is clearly noted the formation of a simple semicircle, with a ca. $32 \ \Omega \text{cm}^2$ diameter associated with the resistance of the charge transfer process, R_{ct} , across the steel-electrolyte interface [8]. The R_{ct} is inversely proportional to the corrosion current density thus, the bigger the R_{ct} the lower the corrosion susceptibility of the material. However, when Pantoprazole is present in the API 5L X52 / HCl 1M interface, see Figures 1b-1e, the impedance spectra changed notoriously due to an increment in the corresponding R_{ct} value. For a constant value of the electrode rotation speed, it can be noted that the R_{ct} value increases as the Pantoprazole concentration does. Notwithstanding, for a fixed Pantoprazole concentration, the R_{ct} value diminishes as the electrode rotation speed increases: this can be clearly noted by comparing the Nyquist plot recorded at 200 ppm Pantroprazol in Figure 1b (0 rpm) with the corresponding one in Figure 1e (1000 rpm).



Figure 1. Nyquist plots recorded in the system a) API 5L X52 / 1 M HCl at 25 °C after adding different Pantoprazole concentrations, indicated in b), and imposing different rotation rates to the working electrode : (b) 0, (c) 40, (d) 100 and (e) 1000 rpm.

Comparing the impedance diagrams recorded at 50 ppm and the different rotation speeds considered in this work, it was found that the R_{ct} values reached were largest when imposing 40 rpm to the working electrode, reaching a maximum value of ca. 480 Ω cm².



Figure 2. Comparison of the Nyquist plots recorded in the system a) API 5L X52 / 1 M HCl, 50 ppm Pantoprazole at 25 °C and different hydrodynamic conditions indicated in the figure.

In order to analyze the experimental Nyquist plots and considering their characteristic features, the typical EECs [6,8,31,32] shown in Figure 3 were used, first for the blank (Figure 3a) and then when Pantoprazole was present in the corrosive media (Figure 3b). The circuit comprises the solution resistance R_s , the charge transfer resistance, R_{ct} , and R_{mol} which is associated with the resistance of the adsorbed inhibitor layer. For the description of a frequency independent phase shift between an applied AC potential and its current response, a constant phase element (*CPE*) is used, which is defined in impedance representation as:

$$Z_{CPE} = Y_0^{-1} (j\omega)^{-n}$$
(1)

where Y_0 is the *CPE* constant, *n* is the *CPE* exponent that can be used as a gauge of the heterogeneity or roughness of the surface, $j^2 = -1$ is an imaginary number and ω is the angular frequency in rad s⁻¹. Depending on *n*, *CPE* can represent a resistance ($Z_{CPE} = R$, n = 0); capacitance ($Z_{CPE} = C$, n = 1), a Warburg impedance ($Z_{CPE} = W$, n = 0.5) or inductance ($Z_{CPE} = L$, n = -1). The correct equation to convert Y_0 into C_{dl} is given by [34].

$$C_{dl} = Y_0 \left(\widetilde{\omega_m} \right)^{-n} \tag{2}$$

 R_{ct}



R_{mo1}

 R_{ct}

where $C_{\rm dl}$ is the double layer capacitance and ω'' is the angular frequency at which $Z_{\rm re}$ is maximum.



Figure 4 shows some examples of the fittings of the EECs, shown in Figure 3, to the experimental data, for the blank, see Figure 4a, and in the presence of 25 ppm of Pantoprazole inhibitor at different rotation speeds of the working electrode, see Figures 4b-4d. In all cases, a good fit can be observed to the experimental data. The values of the electrochemical parameters obtained from Nyquist plots are given in Tables 1-4. The results in the Tables show that R_{ct} increases with increasing inhibitor concentration, corresponding with the increase in the diameter of the semicircles, as mentioned above.

Table 1. Electrochemical parameters obtained during the fitting procedure to the data shown in Figure 1b (0 rpm) with the equivalent electrical circuit "B" shown in Figure 3; for the blank circuit "A" was used.

| C / ppm | R_s / Q cm ² | E _{corr} / mV | n | C_{dl} | R_{ct} | IE / % |
|------------|------------------------------|---------------------------|-----|----------|----------|-----------|
| 0 | 0.8 | -432 | 0.8 | 310 | 30 | - |
| 5 | 0.9 | -429 | 0.8 | 135 | 199 | 85 |
| 10 | 0.9 | -433 | 0.8 | 119 | 288 | 90 |
| 15 | 0.9 | -439 | 0.8 | 108 | 342 | 91 |
| 20 | 0.9 | -451 | 0.8 | 96 | 417 | 93 |
| 25 | 0.9 | -454 | 0.8 | 94 | 423 | 93 |
| 30 | 0.9 | -457 | 0.8 | 91 | 411 | 93 |
| 50 | 0.9 | -460 | 0.8 | 89 | 422 | 93 |
| 80 | 0.9 | -464 | 0.8 | 88 | 409 | 93 |
| 100 | 0.9 | -465 | 0.8 | 89 | 379 | 92 |
| 200 | 0.1 | -431 | 0.9 | 52 | 449 | 93 |

Table 2. Table 1. Electrochemical parameters obtained during the fitting procedure to the data shown in Figure 1c (40 rpm) with the equivalent electrical circuit "B" shown in Figure 3; for the blank circuit "A" was used.

| C / ppm | R_s / Ωcm^2 | E _{corr} / mV | n | C _{dl} / µFcm ² | $\frac{R_{ct}}{/ \Omega cm^2}$ | IE / % |
|------------|-----------------------|---------------------------|-----|--|--------------------------------|-----------|
| 0 | 0.8 | -432 | 0.8 | 310 | 30 | - |
| 5 | 0.7 | -444 | 0.9 | 82 | 153 | 83 |
| 10 | 0.7 | -435 | 0.9 | 72 | 26 | 90.5 |
| 20 | 0.7 | -426 | 0.9 | 61 | 305 | 91.6 |
| 25 | 0.7 | -423 | 0.9 | 60 | 484 | 94.7 |
| 30 | 0.7 | -428 | 0.9 | 62 | 519 | 95.1 |
| 80 | 0.7 | -425 | 0.9 | 57 | 518 | 95.3 |
| 100 | 0.7 | -430 | 0.9 | 52 | 542 | 95.4 |
| 200 | 0.7 | -431 | 0.9 | 52 | 549 | 95.7 |

Table 3. Table 1. Electrochemical parameters obtained during the fitting procedure to the data shown in Figure 1d (100 rpm) with the equivalent electrical circuit "B" shown in Figure 3; for the blank circuit "A" was used.

| С / ррт | R_s / Ω cm ² | E _{corr} / mV | n | C _{dl} / μF cm ² | R_{ct} / Ωcm^2 | IE / % |
|------------|----------------------------------|---------------------------|-----|---|-----------------------------|-----------|
| 0 | 1.4 | -486 | 0.8 | 310 | 30 | - |
| 5 | 0.7 | -421 | 0.6 | 291 | 140 | 78 |
| 10 | 0.7 | -441 | 0.9 | 280 | 156 | 81 |
| 15 | 0.7 | -431 | 0.9 | 134 | 203 | 85 |
| 20 | 0.8 | -431 | 0.8 | 134 | 203 | 85 |
| 25 | 0.7 | -434 | 0.9 | 85 | 234 | 87 |
| 30 | 0.7 | -436 | 0.9 | 83 | 258 | 88 |
| 50 | 0.7 | -439 | 0.8 | 84 | 274 | 89 |
| 80 | 0.7 | -440 | 0.8 | 83 | 284 | 89 |
| 100 | 0.7 | -443 | 0.7 | 81 | 284 | 89 |
| 200 | 0.7 | -444 | 0.7 | 80 | 290 | 89 |

Table 4. Electrochemical parameters obtained during the fitting procedure to the data shown in Figure 1e (1000 rpm) with the equivalent electrical circuit "B" shown in Figure 3; for the blank circuit "A" was used.

| C / ppm | R_s / Ω cm ² | E _{corr} / mV | n | C _{dl} / μF cm ² | $\frac{R_{ct}}{/ \Omega cm^2}$ | IE / % |
|------------|----------------------------------|---------------------------|-----|---|--------------------------------|-----------|
| 0 | 1.4 | -486 | 0.8 | 310 | 30 | - |
| 10 | 0.7 | -426 | 0.9 | 234 | 79 | 68 |
| 15 | 0.7 | -426 | 0.9 | 230 | 85 | 70 |
| 20 | 0.7 | -427 | 0.9 | 203 | 94 | 73 |
| 25 | 0.7 | -428 | 0.8 | 190 | 101 | 75 |
| 30 | 0.7 | -428 | 0.8 | 124 | 110 | 77 |
| 50 | 0.7 | -428 | 0.8 | 136 | 130 | 80 |
| 80 | 0.7 | -430 | 0.8 | 122 | 146 | 83 |
| 100 | 0.8 | -432 | 0.8 | 111 | 160 | 84 |
| 200 | 0.8 | -433 | 0.8 | 104 | 178 | 86 |



Figure 4. Comparison of experimental EIS data (points) measured for pipeline steel samples immersed in 1M HCl and the simulated (line) for all the data shown in Figure 2. (a) the blank, (b) 0, (c) 40, (d) 100 and (e) 1000 rpm.

Equation (3) [1] allows the quantification of the corrosion inhibition efficiency (IE) of the Pantoprazole using the R_{ct} values obtained from the analysis of the experimental impedance plots, see Tables 1-4.

$$IE(\%) = \frac{(1/R_{ct})blank - (1/R_{ct})inhibitor}{(1/R_{ct})blank} X100$$
(3)

Where $R_{ct(inhitor)}$ and $R_{ct(blank)}$ are the charge transfer resistance values with and without inhibitor, respectively.

Figure 5 shows the variation of the corrosion inhibition efficiency of Pantoprazole with its concentration obtained at different rotation speeds. It should be noted that at moderate rotation speeds namely 40 rpm, the convection force produced displayed improved inhibition efficiency at concentrations greater than 25 ppm, which is attributed to the flow of inhibitor molecules transported to the metal surface, thereby giving rise to an adsorbed molecular layer interposing over the metal surface, thus increasing the inhibition efficiency. However, for rotation speeds greater than 40 rpm the opposite can occur.



Figure 5. Variation of the corrosion inhibition efficiency of the Pantoprazole evaluated in the system API 5L X52 / 1 M HCl, x ppm Pantoprazole at 25 °C as a function of [Pantropazole] at different working electrode's rotation speed, indicated in the figure.

3.2 Effect of exposure time.

To pursue the electrochemical study at different concentrations and to relate the results obtained with the demonstrated effectiveness of the Pantoprazole's corrosion inhibiting properties has been achieved on a point basis. However, it would be a more central interest to evaluate the inhibitor's temporal behavior through the kinetics associated to relatively long immersion times. Figure 6 shows the impedance results with values reaching ca. $800 \ \Omega \text{cm}^2$ after 72 h immersion, the impedance spectra clearly depicts two well resolved time constants, one related to the substrate while the other refers to the organic molecules' charge transfer resistance as the EEC used suggests. Table 5 shows the variation of the R_{ct} data derived as a function of the immersion time. From this Table it is possible to note that during the first 24 h the IE increases and then slowly diminishes.



- **Figure 6.** Experimental (markers) and simulated (lines) electrochemical impedance diagrams, Nyquist plots, for pipeline mild steel immersed in HCl in the presence of 25 ppm Pantoprazole, at stagnant conditions and 25 °C, during different immersion times indicated in the figure. The equivalent electric circuit used to obtain the impedance parameters was that shown in Figure 3b.
- **Table 5.** Charge transfer resistance values obtained during the fitting procedure to the data shown in Figures 6 with the equivalent electrical circuit "B" shown in Figure 3. The IE was calculated according with eqn.(3).

| Immersion time /h | $rac{R_{ m ct}}{/\Omega m cm^2}$ | IE / % |
|-------------------------|------------------------------------|-----------|
| 0.5 | 422 | 92.9 |
| 1 | 432 | 93.1 |
| 5 | 529 | 94.3 |
| 24 | 833 | 96.4 |
| 72 | 825 | 96.4 |
| 168 | 730 | 95.9 |
| 240 | 712 | 95.8 |
| 336 | 699 | 95.7 |
| 504 | 541 | 94.5 |
| 672 | 495 | 93.9 |



Figure 7. Variation of the corrosion inhibition efficiency of the Pantoprazole as a function of immersion time evaluated in the system mild steel immersed in HCl in the presence of 25 ppm Pantoprazole at stagnant conditions and 25 °C.

From Figure 7 it is possible to note that for immersion times greater than 24 h, the inhibition efficiency diminishes linearly with immersion time. Notwithstanding, the Pantoprazole can provide adequate (with an IE > 93%) to the steel substrate even after 673 hours exposure to this highly corrosive media.

3.3 Effect of temperature

It has been reported in the literature, that when the temperature increases, the corrosion rate also increases and hence the efficiency of inhibiting organic compounds decreases [22-24]. Therefore, it is also important to evaluate the effect of this variable. Figure 8 show the experimental impedance plots recorded in the system API 5L X52 / 1 M HCl at stagnant conditions, for different Pantoprazole concentrations and a temperature of 40 °C, Figure 8a, and 60 °C, Figure 8b. Moreover, based on the results that showed that the best conditions observed were when the electrode rotated at 40 rpm, therefore, a study was performed using 40 °C and 40 rpm, see Figure 8c, varying the inhibitor concentrations. The values of the electrochemical parameters obtained from Nyquist plots are given in Tables 6-8.



Figure 8. Nyquist plots recorded in the system API 5L X52 / 1 M HCl at different Pantoprazole concentrations, indicated in the figures, and after imposing different temperatures a) 40 and b) 60 °C at stagnant conditions. The Nyquist plots depicted in c) where recorded in the same system at 40 °C and 40 rpm.

| Table | 6. Electrochemical parameters obtained during the fitting procedure to the data shown in Figure |
|-------|---|
| | 8a (40 °C) with the equivalent electrical circuit "B" shown in Figure 3; for the blank circuit |
| | "A" was used. |

| С / ррт | R_s / Ωcm^2 | E _{corr} / mV | n | R_{ct} / Ωcm^2 | IE / % |
|------------|-----------------------|---------------------------|-----|--------------------------|-----------|
| 0 | 0.8 | -432 | 0.8 | 30 | - |
| 5 | 0.8 | -488 | 0.8 | 90 | 67 |
| 10 | 0.8 | -501 | 0.8 | 101 | 70 |
| 15 | 0.8 | -510 | 0.9 | 98 | 69 |
| 20 | 0.9 | -522 | 0.9 | 98 | 69 |
| 25 | 0.9 | -516 | 0.8 | 100 | 70 |
| 30 | 0.9 | -513 | 0.8 | 96 | 69 |
| 50 | 0.9 | -516 | 0.8 | 105 | 72 |
| 80 | 1.0 | -519 | 0.8 | 102 | 71 |
| 100 | 1.0 | -511 | 0.8 | 97 | 69 |
| 200 | 1.0 | -503 | 0.8 | 97 | 69 |

Table 7. Electrochemical parameters obtained during the fitting procedure to the data shown in Figure 8b (60 °C) with the equivalent electrical circuit "B" shown in Figure 3; for the blank circuit "A" was used.

| C / ppm | R_s / Ωcm^2 | E _{corr} / mV | n | R _{ct} / Ωcm ² | IE / % |
|------------|-----------------------|---------------------------|-----|---------------------------------------|-----------|
| 0 | 0.8 | -432 | 0.8 | 30 | - |
| 5 | 0.8 | -436 | 0.8 | 50 | 41 |
| 10 | 0.8 | -479 | 0.9 | 52 | 42 |
| 15 | 0.8 | -480 | 0.9 | 63 | 53 |
| 20 | 0.9 | -483 | 0.8 | 66 | 55 |
| 25 | 0.9 | -505 | 0.8 | 66 | 54 |
| 30 | 0.9 | -495 | 0.8 | 66 | 55 |
| 50 | 0.8 | -502 | 0.8 | 65 | 54 |
| 80 | 1.0 | -504 | 0.8 | 65 | 54 |
| 100 | 1.0 | -507 | 0.8 | 68 | 57 |
| 200 | 0.8 | 509 | 0.9 | 68 | 57 |

Table 8. Electrochemical parameters obtained during the fitting procedure to the data shown in Figure 8c (40 °C and 40 rpm) with the equivalent electrical circuit "B" shown in Figure 3; for the blank circuit "A" was used.

| C / ppm | R_s / Ω cm ² | E _{corr} / mV | n | R _{ct} / Ωcm ² | IE / % |
|------------|----------------------------------|---------------------------|-----|---------------------------------------|-----------|
| 0 | 0.8 | -432 | 0.8 | 30 | - |
| 5 | 0.6 | -474 | 0.8 | 77 | 61 |
| 10 | 0.6 | -487 | 0.8 | 101 | 70 |
| 15 | 0.7 | -487 | 0.8 | 99 | 70 |
| 20 | 0.7 | -493 | 0.9 | 125 | 71 |
| 25 | 0.7 | -497 | 0.8 | 124 | 71 |
| 30 | 0.7 | -502 | 0.9 | 125 | 71 |
| 50 | 0.8 | -504 | 0.8 | 125 | 71 |
| 80 | 1.2 | -487 | 0.8 | 130 | 74 |
| 100 | 0.7 | -509 | 1.0 | 131 | 75 |
| 200 | 1.3 | -508 | 0.8 | 138 | 78 |

From Figure 9 it is possible to note that for a given Pantoprazole concentration its corrosion inhibition efficiency diminish as the temperature of the electrolyte increases.



Figure 9. Variation of the corrosion inhibition efficiency of Pantoprazole evaluated in the system API 5L X52 / 1 M HCl, x ppm Pantoprazole at different temperatures indicated in the figure.

3.4 Inhibition mechanism

The adsorption isotherms provide basic information on the interaction between the organic compound studied and the metal surface. Two types of adsorption describe such interaction, namely, physisorption and chemisorption. The physisorption process reflects the type of interaction with Van der Waals forces between the molecules of adsorbed inhibitor and the metal surface with values below -20 KJ mol⁻¹. However, for the chemisorption process, the interaction involves sharing charges and coordinate bond formation between the steel surface and the organic molecules with values above -40 KJ mol⁻¹ [12-17].

Then, Figure 10a shows as result, the corresponding fitting to the data from each of the rotation speeds studied at 20 °C; a good fit of the Langmuir expression, as described by Equation 4, to the experimental data was observed.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{4}$$

Where C is the inhibitor concentration, K_{ads} is the adsorption constant and θ the coverage degree.

The regression plot of C/ θ vs. C was fitted to the experimental data, thus giving a straight line, as indicated in Figure 10a, which is typical of the Langmuir adsorption isotherm at different temperatures, see equation (4) with a Gibbs free energy of absorption, ΔG°_{ads} , estimated by means of the equation (5) [8].

$$\Delta G^{\circ} = -RT lnk_{ads} \tag{5}$$

Closely linear plots were obtained in all cases with correlation coefficients of 0.99 and slope values near to 1, see Table 9, at different conditions. The standard free energy of adsorption, ΔG^{o}_{ads} , which can characterize the molecules' adsorption interaction with the metal surface, were calculated through eqn. (4) and are reported in Table 9. From the latter it is possible to note that ΔG^{o}_{ads} , values are lower than -16 kJ.mol⁻¹, therefore, in this case the adsorption type of all the inhibitors tested can be classed as physisorption.



Figure 10. Comparison between the experimental adsorption isotherm (points) for Pantoprazole on API 5L X52 steel in 1M HCl at a) different temperatures, indicated in the figure, and stagnant conditions and b) 40°C and 40 rpm with the theoretical model (lines) proposed by Langmuir, equation (4).

Table 9. Estimation of the adsorption constant (K_{ads}) and the standard free energy of adsorption (ΔG^{o}_{ads}) for different rotation speeds at room temperature tested in the system API 5L X52 steel in 1M HCl: the Langmuir model was fitted to the experimental isotherms.

| Rotation | Temperature | Linear regression equation | lnK _{ads} | ΔG°_{ads} | \mathbf{R}^2 |
|----------|-------------|-----------------------------------|--------------------|--------------------------|----------------|
| Speed/ | ∕°C | | | (KJ/mol) | |
| rpm | | | | | |
| 0 | 25 | C/O [mM]=1.08 C [mM] + 0.001 [mM] | 6.90 | -16.83 | 0.9999 |
| 40 | 25 | C/O [mM]=1.05 C [mM] + 0.005 [mM] | 5.29 | -12.91 | 0.9986 |
| 100 | 25 | C/O [mM]=1.11 C [mM] + 0.008 [mM] | 4.85 | -11.82 | 0.9983 |
| 1000 | 25 | C/Θ [mM]=1.18 C [mM] + 0.036 [mM] | 3.32 | -8.11 | 0.99 |
| 0 | 40 | C/O [mM]=1.34 C [mM] + 0.024 [mM] | 3.74 | -9.75 | 0.9999 |
| | | | | | |
| 0 | 60 | C/O [mM]=1.85 C [mM] + 0.009 [mM] | 4.65 | -12.89 | 0.9983 |
| | | | | | |
| 40 | 40 | C/O [mM]=1.27 C [mM] + 0.029 [mM] | 3.41 | -9.16 | 0.9986 |

4. CONCLUSIONS

It has been shown that Pantoprazole is a green corrosion inhibitor for mild steel immersed in 1 M HCl at 25 °C, displaying an adequate performance at different hydrodynamic conditions and immersion times, even at rather low concentrations, namely 25 ppm. In accordance to the thermodynamic analysis performed, the Pantoprazole corrosion inhibition occurs through a physisorption process. When the temperature increased, the IE of the system was adversely affected, since it decreased considerably.

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