

Full Paper

Anti-corrosion Properties of some Triphenylimidazole Substituted Compounds in Corrosion Inhibition of Carbon Steel in 1.0 M Hydrochloric Acid Solution

Mouhsine Galai,¹ Mohamed Rbaa,² Younes El Kacimi,^{1,*} Moussa Ouakki,³ Nadia Dkhirech,¹ Rachid Tourir,^{1,4} Brahim Lakhrissi² and Mohamed Ebn Touhami¹

¹*Laboratory of Materials Engineering and Environment: Modeling and Application, Faculty of Science, University Ibn Tofail BP. 133-14000, Kenitra, Morocco*

²*Laboratory of Polymers, Radiation and Environment- Team of Macromolecular & Organic Chemistry, Faculty of Science, University Ibn Tofail, Kenitra, Morocco*

³*Laboratory of Materials, Electrochemistry and Environment, Faculty of Science, Ibn Tofail University, Kénitra, Morocco*

⁴*Centre Régional des métiers de l'éducation et de la formation (CRMEF), Avenue Allal Al Fassi, Madinat Al Irfane, BP 6210 Rabat, Morocco*

*Corresponding Author, Tel.: +212 663566545

E-Mail: elkacimiyounes@yahoo.fr

Received: 14 November 2016 / Received in revised form: 11 December 2016 /

Accepted: 24 December 2016 / Published online: 15 February 2017

Abstract- Two triphenylimidazole substituted compounds, namely 2,4,5-triphenyl-4,5-dihydro-1H-imidazole (P1) and 2-(4,5-diphenyl-4,5-dihydro-1H-imidazol-2-yl)phenol (P2) were studied as inhibitors for the corrosion of carbon steel in 1.0 M hydrochloric acid (HCl) solution has been examined and characterized by weight loss, Tafel polarization and electrochemical impedance spectroscopy (EIS). It was found that the studied compounds exhibit a very good performance as inhibitors for carbon steel corrosion in 1.0 M HCl. Results show that the inhibition efficiency increases with decreasing temperature and increasing concentration of inhibitors. Good agreement between the results obtained from weight loss and electrochemical measurements. It has been determined that the adsorption for the studied inhibitors on carbon steel complies with the Langmuir adsorption isotherm at all studied temperatures. The kinetic and thermodynamic parameters for carbon steel corrosion

and inhibitor adsorption, respectively, were determined and discussed. On the bases of thermodynamic adsorption parameters, comprehensive adsorption (physisorption and chemisorption) for the studied inhibitors on mild steel surface was suggested. Results show that the order of inhibition efficiency is $P2 > P1$ due to presence of electron donating hydroxyl (-OH) groups in P2. Potentiodynamic polarization studies have shown that compounds studies acts as a mixed type of inhibitor's. Scanning electron microscopy (SEM) was performed and discussed for surface study of uninhibited and inhibited carbon steel samples.

Keywords- Inhibitor, substituted Triphenylimidazole compounds, Carbon steel, Hydrochloric acid, Adsorption isotherm, EIS

1. INTRODUCTION

Mild steel has been widely used as a main construction material for piping works in various industries. It has found applications in downhole casing or tubing, flow lines and transmission or distribution pipelines in oil and gas industries [1-3]. Petroleum oil well acidization is an essential technique that is routinely used in oil and gas industries for the purpose of stimulating oil-well to ensure enhanced oil production [4,5]. This process however endangers the life of steel gadgets as a result of acid driven corrosion. In order to prevent this undesirable reaction, corrosion inhibitors are often added to the acid solution during acidification process [6-8].

These compounds inhibit corrosion by adsorbing on metallic surface using heteroatoms (e.g. N, O, S), polar functional groups (e.g. -OH, -NH₂, -NO₂, etc.), pi-electrons and aromatic rings as adsorption centers [9-11]. Inhibitors retard metal corrosion by adsorbing on metallic surface and the process is influenced by some factors, which include molecular size of inhibitor, nature of substituents, inhibitor concentration, solution temperature and nature of test solution. [8,9,11]

These compounds can form either a strong coordination bond with metal atom or a passive film on the surface [12]. The corrosion inhibition of a metal may involve either *physisorption* or *chemisorption* of the inhibitor on the metal surface. Electrostatic attraction between the charged hydrophilic groups and the charged active centers on the metal surface leads to *physicosorption*. Several authors showed that most inhibitors were adsorbed on the metal surface by displacing water molecules from the surface and forming a compact barrier film [13].

Perusal of literature reveals that many N-heterocyclic compounds such as pyrimidine derivatives [14], triazole derivatives [15], tetrazole derivatives [16], phenyltetrazole derivatives [7], pyrazole derivative [17], bipyrazole derivatives [18], indole derivatives [19], pyridazine derivatives [20], benzimidazole derivatives [21] to mention but a few, have been used for the corrosion inhibition of iron or steel in acidic media. Imidazole is an organic compound which has a heterocyclic structure with molecular formula of C₃H₄N₂. Imidazole compound and its derivatives contain N functional groups with lone pairs electrons and the

resonance system within the aromatic ring that facilitates their interaction with carbon steel surface. Many imidazole derivative compounds have been synthesized because of their low toxicity and environmentally friendly properties [22]. Imidazoles are a class of heterocyclic compounds that contain nitrogen and are currently under intensive focus due to their wide range of applications [23]. Synthetic study of imidazole units is very important due to their potent biological activity [24] and synthetic utility [25]. Imidazoles are an important class of heterocycles being the core fragment of different natural products and biological systems. Compounds containing imidazole moiety have many pharmacological properties and play important roles in biochemical processes [26]. The potency and wide applicability of the imidazole pharmacophore can be attributed to its hydrogen bond donor-acceptor capability as well as its high affinity for metals (e.g., Zn, Fe, Mg), which are present in many protein active sites 3b [27,28].

The purpose of this paper is to investigate the corrosion inhibition capability of *substituted Triphenylimidazole compounds* against the corrosion of carbon steel in 1.0 M HCl solution. Corrosion inhibition was studied using weight loss, electrochemical impedance spectroscopic (EIS) and potentiodynamic polarization methods (Tafel). The adsorption and inhibition efficiency of these inhibitor were investigated and the thermodynamic adsorption parameters in absence and presence of *substituted Triphenylimidazole* were calculated. The effect of temperature on the corrosion behavior was also studied in the range from 25±2 °C to 55±2 °C. The thermodynamic parameters such as adsorption heat ΔH_a^* , entropy of adsorption ΔS_a^* and adsorption free energy ΔG_a^* were calculated and discussed. Scanning electron microscopy (SEM) was performed and discussed for surface study of uninhibited and inhibited carbon steel samples.

2. EXPERIMENTAL TECHNIQUES

2.1. Materials preparation

The chemical composition of steels sample is shown in Table 1. The specimen's surface was prepared by polishing with emery paper at different grit sizes (from 180 to 1200), rinsing with distilled water, degreasing in ethanol, and drying at hot air.

Corrosion tests were performed on carbon steel which had the following chemical composition (wt %) balanced with Fe.

Table 1. Chemical composition of low carbon steel used

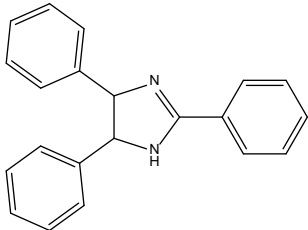
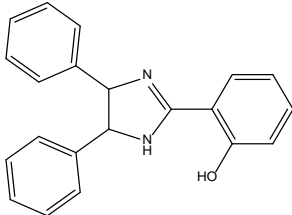
| <i>Material</i> | <i>Composition, % by wt</i> | | | | | | | | | | | |
|-----------------|-----------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----------|----------|-----------|
| | <i>C</i> | <i>Si</i> | <i>Mn</i> | <i>Cr</i> | <i>Mo</i> | <i>Ni</i> | <i>Al</i> | <i>Cu</i> | <i>Co</i> | <i>V</i> | <i>W</i> | <i>Fe</i> |
| Carbon steel | 0.11 | 0.24 | 0.47 | 0.12 | 0.02 | 0.1 | 0.03 | 0.14 | <0.0012 | <0.003 | 0.06 | Balance |

The steels specimens used have a rectangular form 2.5 cm×2.0 cm×0.05 cm. The immersion time for weight loss was 6 h at 25±2 °C. After immersion period, the specimens were cleaned according to ASTM G-81 and reweighed to 10⁻⁴ g for determining corrosion rate [29].

The aggressive solution of 1.0 M HCl was prepared by dilution of analytical grade 37% HCl with distilled water.

The molecular formula of the examined inhibitor is shown in Table 2.

Table 2. Names, chemical structures and abbreviations of the studied Imidazole compounds

| <i>Abbreviation</i> | <i>Chemical structure</i> | <i>IUPAC Name / molecular formula / Molar mass</i> |
|---------------------|---|--|
| P1 |  | 2,4,5-triphenyl-4,5-dihydro-1H-imidazole <hr/> <chem>C21N2H16</chem> <hr/> 296.37 |
| P2 |  | 2-(4,5-diphenyl-4,5-dihydro-1H-imidazol-2-yl)phenol <hr/> <chem>C21H16N2O</chem> <hr/> 312.36 |

2.2. Corrosion weight loss tests

Weight loss experiments were done according to ASTM methods described previously. Tests were conducted in 1.0 M HCl for 6 h at 25±2 °C. Gravimetric measurements were carried out in an electrolysis cell equipped with a thermostat-cooling condenser. The carbon steel specimens used have a rectangular form 2.5 cm×2.0 cm × 0.05 cm. After immersion period, the specimens were cleaned according to ASTM G-81 and reweighed to 10⁻⁴ g for determining corrosion rate [29]. Duplicate experiments are performed in each case, and the mean value of the weight loss is reported. Weight loss allows us to calculate the mean corrosion rate as expressed in (mg.cm⁻².h⁻¹). The resulting quantity, corrosion rate (ω_{corr}) is thereby the fundamental measurement in corrosion. (ω_{corr}) can be determined either by chemical analysis of dissolved metal in solution or by gravimetric method measuring

weight of specimen before and after exposure in the aggressive solution applying the following equation 1:

$$\omega_{corr} = \frac{m_i - m_f}{St} \quad (1)$$

Where m_i , m_f , S and t denote initial weight, final weight, surface of specimen and immersion time, respectively.

The inhibition efficiency, $\eta_{\omega}\%$, is determined as follows:

$$\eta_{\omega} \% = \frac{\omega_{corr}^0 - \omega_{corr}}{\omega_{corr}^0} \times 100 \quad (2)$$

Where ω_{corr}^0 and ω_{corr} are the corrosion rates in the absence and presence of inhibitors, respectively.

2.3. Electrochemical cell

2.3.1. Potentiodynamic polarization measurement

For electrochemical measurements, the electrolysis cell was a borosilicate glass (Pyrex[®]) cylinder closed by a cap with five apertures. Three of them were used for the electrode insertions. The working electrode was pressure-fitted into a polytetrafluoroethylene holder (PTFE) exposing only 1cm² of area to the solution. Platinum and saturated calomel were used as counter and reference electrode (SCE), respectively. All potentials were measured against the last electrode.

The potentiodynamic polarization curves were recorded by changing the electrode potential automatically from negative values to positive values versus E_{corr} using a Potentiostat/Galvanostat type PGZ 100, at a scan rate of 1 mV/s after 1 h of immersion time until reaching steady state. The test solution was thermostatically controlled at 25±2 °C in air atmosphere without bubbling. To evaluate corrosion kinetic parameters, a fitting by Stern-Geary equation was used. To do so, the overall current density values, i , were considered as the sum of two contributions, anodic and cathodic current i_a and i_c , respectively. For the potential domain not too far from the open circuit potential, it may be considered that both processes followed the Tafel law [24]. Thus, it can be derived from equation (3):

$$i = i_a + i_c = i_{corr} \left\{ \exp[b_a \times (E - E_{corr})] - \exp[b_c \times (E - E_{corr})] \right\} \quad (3)$$

Where i_{corr} is the corrosion current density (A cm⁻²), b_a and b_c are the Tafel constants of anodic and cathodic reactions (V⁻¹), respectively. These constants are linked to the Tafel slopes β (V/dec) in usual logarithmic scale given by equation (4):

$$\beta = \frac{\ln 10}{b} = \frac{2.303}{b} \quad (4)$$

The corrosion parameters were then evaluated by means of nonlinear least square method by applying equation (3) using Origin software. However, for this calculation, the potential range applied was limited to ± 0.100 V around E_{corr} , else a significant systematic divergence was sometimes observed for both anodic and cathodic branches.

The corrosion inhibition efficiency is evaluated from the corrosion current densities values using the relationship (5):

$$\eta_{\text{PP}} = \frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0} \times 100 \quad (5)$$

The surface coverage values (θ) have been obtained from polarization curves for various concentrations of inhibitor using the following equation [30]:

$$\theta = 1 - \frac{i_{\text{corr}}}{i_{\text{corr}}^0} \quad (6)$$

Where i_{corr}^0 and i_{corr} are the corrosion current densities values without and with inhibitor, respectively.

2.3.2. Electrochemical impedance spectroscopy measurements (EIS)

The electrochemical impedance spectroscopy measurements were carried out using a transfer function analyzer (VoltaLab PGZ 100), with a small amplitude a.c. signal (10 mV rms), over a frequency domain from 100 kHz to 100 mHz with five points per decade. The EIS diagrams were done in the Nyquist representation. The results were then analyzed in terms of an equivalent electrical circuit using Bouckamp program [31].

The inhibiting efficiency derived from EIS, η_{EIS} is also added in Table 5 and calculated using the following equation (7):

$$\eta_{\text{EIS}} = \frac{R_{\text{ct}} - R_{\text{ct}}^0}{R_{\text{ct}}} \times 100 \quad (7)$$

Where R_{ct}^0 and R_{ct} are the charge transfer resistance values in the absence and in the presence of inhibitor, respectively.

In order to ensure reproducibility, all experiments were repeated three times. The evaluated inaccuracy did not exceed 10%.

3. RESULTS AND DISCUSSION

3.1. Gravimetric measurements

The effect of different concentration of substituted Triphenylimidazole compounds on the inhibition of carbon steel corrosion in 1.0 M HCl was studied using gravimetric method due

to its simplicity and good reliability. The observed weight-loss values of triplicate measurements are highly reproducible giving standard deviations. The inhibition efficiency ($\eta\%$) and other parameters such as corrosion rate (ω) and surface coverage (θ) at various concentration of the inhibitors are given in Table 3.

Table 3. Weight loss data of carbon steel in 1.0 M HCl without and with different concentrations of substituted Triphenylimidazole compounds at 25 ± 2 °C after 6 h of immersion

| Concentration of inhibitors (M) | P1 | | | P2 | | |
|------------------------------------|---|---------------------------|---------------|---|---------------------------|---------------|
| | $\omega_{corr/P1}$ ($mg\ cm^{-2}\ h^{-1}$) | $\eta_{\omega,P1}$ (%) | θ_{P1} | $\omega_{corr/P2}$ ($mg\ cm^{-2}\ h^{-1}$) | $\eta_{\omega,P2}$ (%) | θ_{P2} |
| 0 | 31.1 | - | - | 31.1 | - | - |
| 10^{-6} | 13.3 | 57.2 | 0.572 | 4.3 | 86.2 | 0.862 |
| 10^{-5} | 9.02 | 71.0 | 0.710 | 2.1 | 93.2 | 0.932 |
| 10^{-4} | 4.2 | 86.5 | 0.865 | 1.3 | 95.8 | 0.958 |
| 10^{-3} | 2.4 | 92.3 | 0.923 | 0.9 | 97.1 | 0.971 |

It is observed that P2 is most efficient among all the tested inhibitors. Careful examination of the results showed that protection efficiencies of the studied inhibitors increase with increasing concentrations. Maximum values of (inhibition efficiency) 92.3% for P1 and 97.1% for P2 were obtained at 10^{-3} M. The inhibitors are expected to get adsorbed through the lone pairs of electrons on N atoms of amino group and imidazole ring as well as π -electron density on the phenyl and imidazole ring by their coordination with metal surface. The participation of phenyl ring in addition to that of N atom during the adsorption process may be confirmed by changing the π -electron density on phenyl ring by substituting electron donating (-OH) group. Generally, electron donating groups increase the inhibition efficiency of the inhibitors. The inhibitors P1 and P2 have nearly same size and number of active centers but P2 shows higher inhibition efficiency ($\eta\%$) than P1 due to higher delocalized π -electron density at benzene ring.

3.3. Potentiodynamic polarization curves

Potentiodynamic polarization curves of carbon steel in 1.0 M HCl without and with different concentrations of all substituted *Triphenylimidazole* compounds are presented in Figure 1. Their extrapolation parameters and inhibition efficiency are plotted in Table 4. It can be shown that the *Triphenylimidazole* addition hinders the acid attack on carbon steel. In addition, an increase in their concentration gives a decrease in anodic and cathodic current

densities indicating that the substituted quinolone compounds acts as mixed-type inhibitors. However, the inhibitor addition does not change the hydrogen evolution reaction mechanism such as indicated by the slight changes in the cathodic slopes (β_c) values. This indicates that hydrogen evolution is activation controlled [32,33]. It is apparent also that the η_{PP} followed the order: P2>P1 such as found by the weight loss measurements. The results obtained by the potentiodynamic polarization curves confirm those obtained by weight loss measurements.

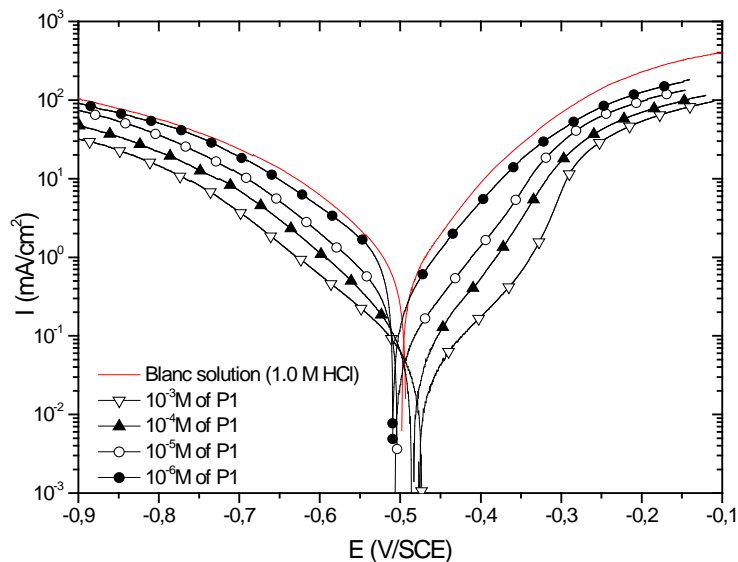


Fig. 1. Potentiodynamic polarization curves for carbon steel in 1.0 M HCl in the absence and presence of various concentrations of P1

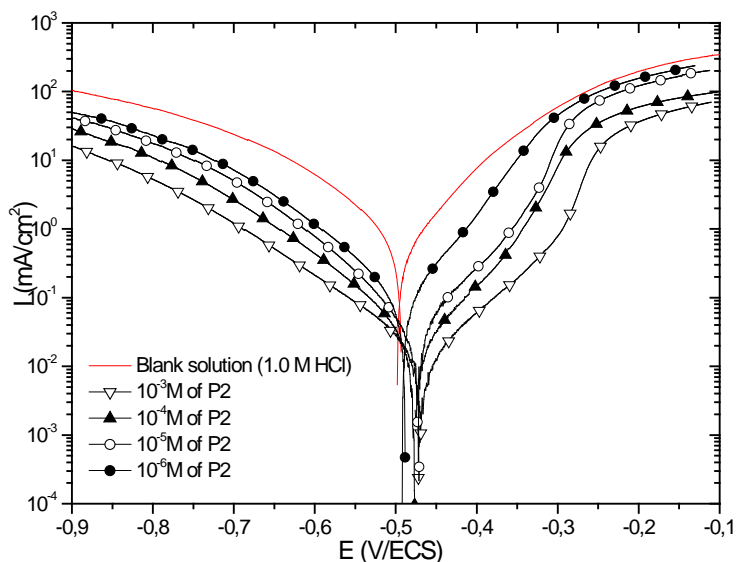


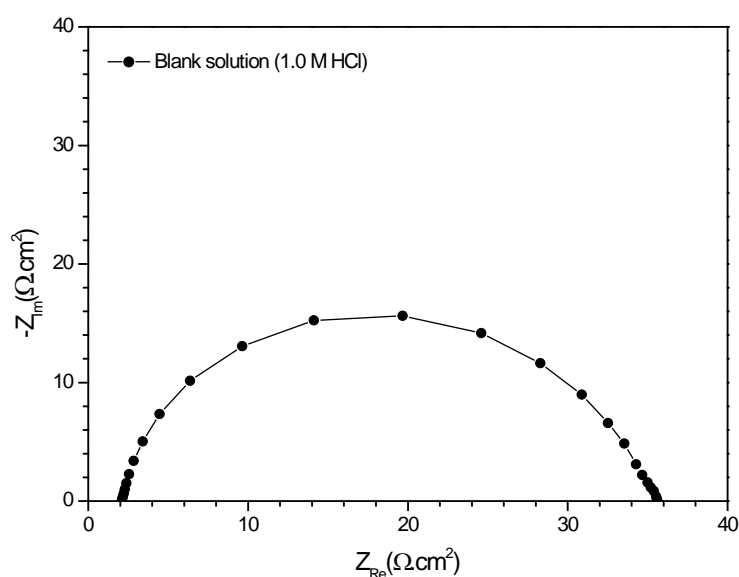
Fig. 2. Potentiodynamic polarization curves for carbon steel in 1.0 M HCl in the absence and presence of various concentrations of P2

Table 4. Electrochemical parameters for carbon steel in 1.0 M HCl at various concentrations of Triphenylimidazole at 25±2 °C

| <i>Compounds</i> | <i>Concentration</i> (M) | <i>E_{corr}</i> (mV vs. SCE) | <i>i_{corr}</i> (mA cm ⁻²) | <i>β_c</i> (mV dec ⁻¹) | <i>β_a</i> (mV dec ⁻¹) | <i>η_{Tafel}</i> (%) |
|------------------|-----------------------------|---|---|---|---|---------------------------------|
| <i>Blank</i> | ----- | -498 | 983 | -92 | 104 | - |
| <i>P1</i> | 10 ⁻⁶ | -505 | 430 | -125 | 55 | 56.3 |
| | 10 ⁻⁵ | -499 | 300 | -129 | 60 | 69.5 |
| | 10 ⁻⁴ | -480 | 130 | -120 | 72 | 86.7 |
| | 10 ⁻³ | -465 | 70 | -108 | 79 | 92.9 |
| <i>P2</i> | 10 ⁻⁶ | -485 | 145 | -78 | 62 | 85.2 |
| | 10 ⁻⁵ | -465 | 50 | -85 | 68 | 94.9 |
| | 10 ⁻⁴ | -473 | 40 | -94 | 74 | 95.9 |
| | 10 ⁻³ | -462 | 25 | -119 | 82 | 97.5 |

3.4. Electrochemical Impedance Spectroscopy (EIS)

Figures 3, 4 and 5 show the Nyquist plots obtained for carbon steel in 1.0 M HCl without and with different concentrations of substituted Triphenylimidazole compounds at the open circuit potential. Their corresponding parameters which were extracted using the equivalent circuit presented in Figures 6, are shown in Table 5. Thus circuit has been used previously to model the iron/acid solution interface [34].

**Fig. 3.** Nyquist plots for carbon steel in 1.0 M HCl solution without inhibitors at 25±2 °C

It is apparent that the obtained spectra were composed of one capacitive loop which its diameter was significantly increased after inhibitors addition to reach a maximum at 10^{-3} M of all compounds. In addition, these diagrams are not perfect semicircles which has been attributed to frequency dispersion [35].

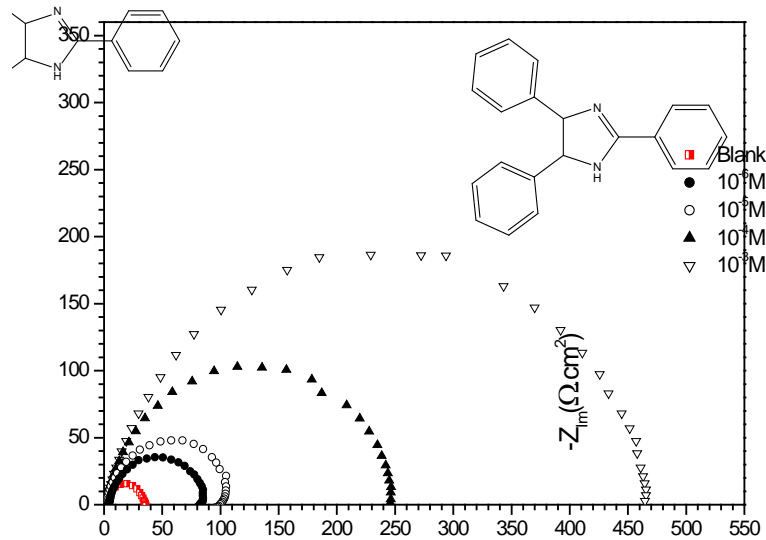


Fig. 4. Nyquist plots for carbon steel in 1.0 M HCl solution in the absence and presence of various concentrations of P1 at 25 ± 2 °C

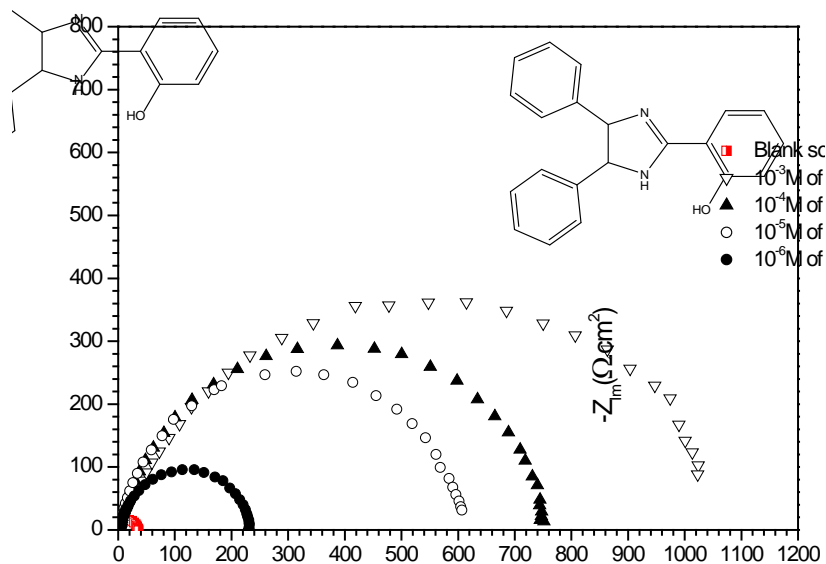


Fig. 5. Nyquist plots for carbon steel in 1.0 M HCl solution in the absence and presence of various concentrations of P2 at 25 ± 2 °C

However, the inhibitors addition is found to enhance R_{ct} values and bring down C_{dl} values. These finding can be explained by the fact that the carbon steel corrosion in 1.0 M HCl was controlled by a charge transfer process and the corrosion inhibition occurs by the adsorption of the substituted Triphenylimidazole compounds on carbon steel surface. However, the decrease in the C_{dl} values, with can result from a decrease in local dielectric constant and/or an increase in courant density, the thickness of the electrical double layer, suggested by adsorption of the Triphenylimidazole molecules at the metal/solution interface [36,37]. It is noted also that the inhibition efficiency follow the order: P2>P1, which is in a good agreement with results obtained from weight loss and potentiodynamic polarization measurements.

Table 5. Electrochemical impedance parameters and inhibition efficiency for carbon steel in 1.0 M HCl solution without and with different concentration of Triphenylimidazole at 25±2 °C

| <i>Compounds</i> | <i>Conc. / M</i> | $R_{ct}/\Omega\text{ cm}^2$ | $C_{ct}/\mu\text{F cm}^{-2}$ | n_{ct} | $\eta_{EIS}/\%$ |
|------------------|------------------|-----------------------------|------------------------------|----------|-----------------|
| <i>Blank</i> | 0 | 35 | 298 | 0.79 | - |
| <i>P1</i> | 10^{-6} | 80 | 90 | 0.87 | 56.2 |
| | 10^{-5} | 110 | 72 | 0.90 | 68.2 |
| | 10^{-4} | 245 | 65 | 0.94 | 85.7 |
| | 10^{-3} | 467 | 54 | 0.95 | 92.5 |
| <i>P2</i> | 10^{-6} | 230 | 90 | 0.76 | 84.8 |
| | 10^{-5} | 611 | 74 | 0.86 | 94.3 |
| | 10^{-4} | 756 | 65 | 0.88 | 95.4 |
| | 10^{-3} | 1089 | 58 | 0.89 | 96.8 |

In the other hand, the effectiveness of organic compounds mainly depends on their size and their active centers [30]. The best performance of compound P2 as corrosion inhibitors over compound P1 may be attributed to the presence of –OH group in compound P2. Indeed, the protection efficiency increases with increasing of inhibitor concentration, the maximum $\eta_{EIS}(\%)$ of 96.8% for P2 was achieved at 10^{-3} M.

Figure 7 (a) and (b) shows Nyquist plots and the representative Bode diagrams for carbon steel in 1.0 M HCl in the presence of various concentrations of 10^{-3} M of P2 to the aggressive solution leads to a change of the impedance diagrams in both shape and size, in which a depressed semicircle at the high frequency part of the spectrum was observed. The increase in size of the semicircle with inhibitor concentration means that the inhibitor effect increases as well.

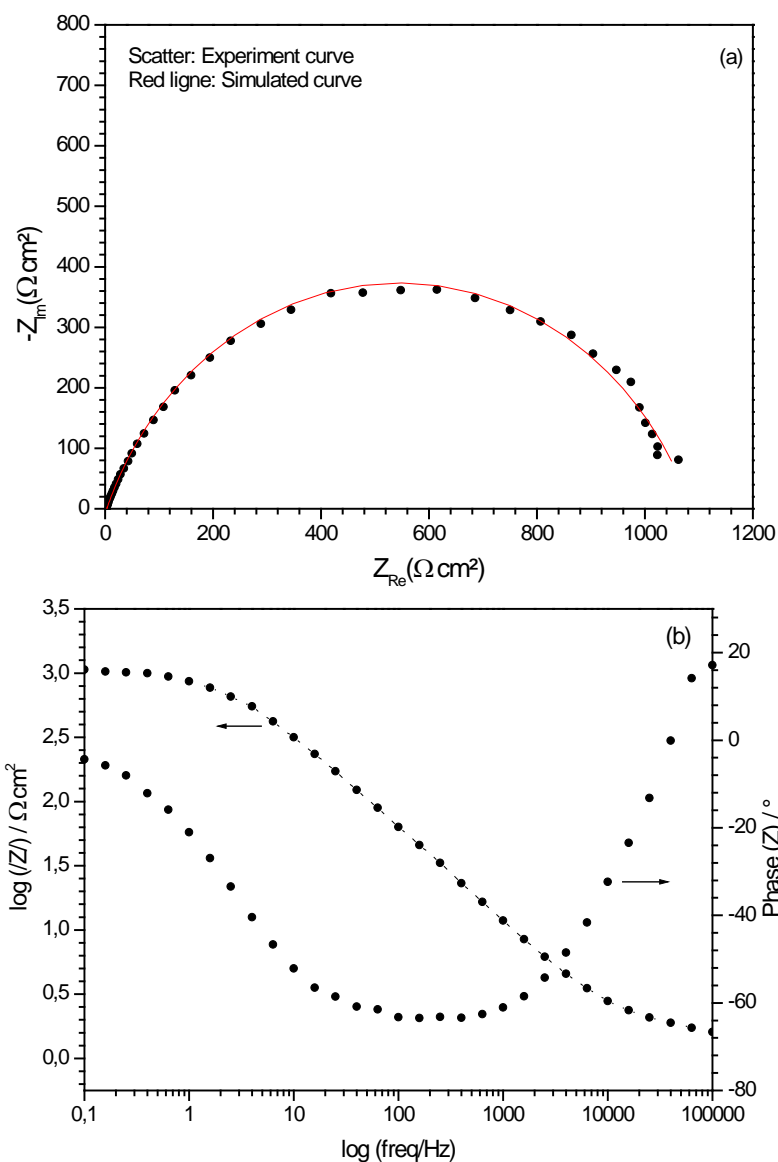


Fig. 7. EIS Nyquist and Bode diagrams for carbon steel/1.0 M HCl with 10^{-3} M of P2 interface: (···) experimental; (—) fitted data using structural model in Fig. 6

Values of the charge transfer resistance R_{ct} were obtained from these plots by determining the difference in the values of impedance at low and high frequencies [38]. The effective capacity C_{dl} can be estimated using the following mathematical formulas from the CPE:

$$C = Q^{1/n_{ct}} * R^{(1-n_{ct})/n_{ct}} \quad (8)$$

With n_{ct} is the degree of heterogeneity.

The equivalent circuit model employed for these systems is presented in figure 6.

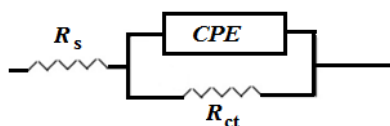


Fig. 6. Equivalent circuit model for system mild steel/1.0 M HCl/Triphenylimidazole Substituted compounds

The results described below can be interpreted in terms of the equivalent circuit of the electrical double layer shown in fig. 6, which has been used previously to model the iron-acid interface [39]. In this equivalent circuit, R_s is the solution resistance, R_{ct} is the charge transfer resistance and CPE is a constant phase element. Excellent fit with this model was obtained for all experimental data. As an example, the Nyquist and Bode plots for 1.0 M HCl solution at 10^{-3} M with P2 are presented in Fig. 7.

3.5. Effect of temperature

Temperature can modify the interaction between the steel electrode and the acidic media without and with substituted quinolone compounds inhibitor's. Polarization curves for carbon steel in 1.0 M HCl in the absence and presence of 10^{-3} M of Triphenylimidazole inhibitor's in the temperature range 25 ± 2 °C to 55 ± 2 °C are shown in Figures 8 to 10 presented the obtained potentiodynamic polarization curves and their corresponding data are presented in Table 6.

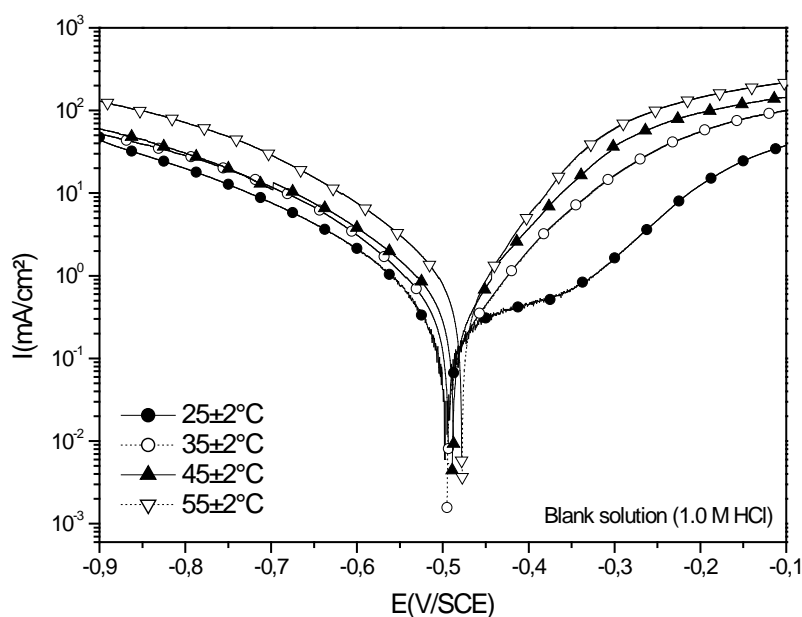


Fig. 8. Potentiodynamic polarization curves for carbon steel in 1.0 M HCl in the absence of inhibitors at different temperatures between 25 ± 2 and 55 ± 2 °C

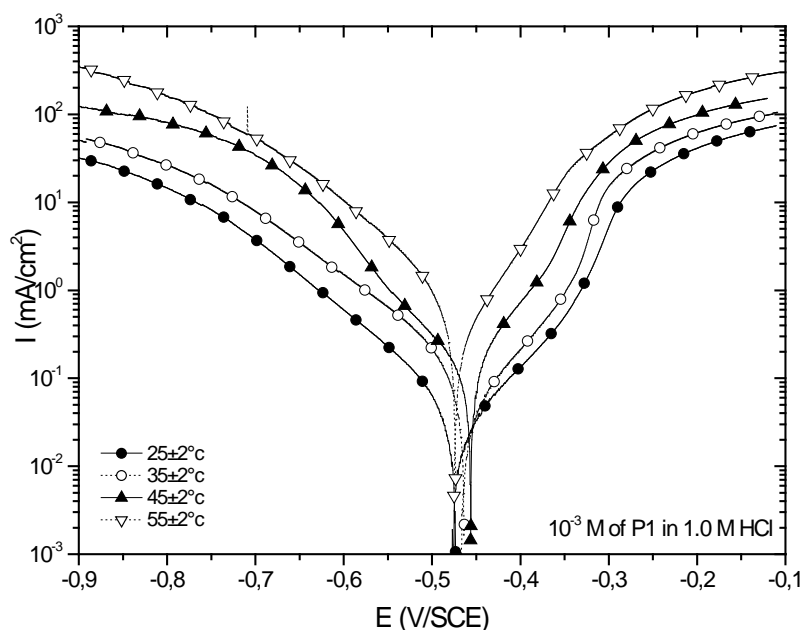


Fig. 9. Potentiodynamic polarization curves for carbon steel in 1.0 M HCl in the presence of 10^{-3} M of P1 at different temperatures between 25 ± 2 °C and 55 ± 2 °C

Table 7. The influence of temperature on the electrochemical parameters for carbon steel in 1.0 M HCl with 10^{-3} M of substituted Triphenylimidazole compounds

| <i>Inhibitors</i> | <i>Temperature</i> (°C) | E_{corr} (mV/SCE) | I_{corr} (mA/cm ²) | β_c (mV) | β_a (mV) | η_{ct} (%) |
|-------------------|----------------------------|------------------------|-------------------------------------|----------------|----------------|-----------------|
| <i>Blank</i> | 25±2 | -498 | 983 | -92 | 104 | - |
| | 35±2 | -491 | 1200 | -184 | 112 | - |
| | 45±2 | -475 | 1450 | -171 | 124 | - |
| | 55±2 | -465 | 2200 | -161 | 118 | - |
| <i>P1</i> | 25±2 | -465 | 70 | -108 | 79 | 92.9 |
| | 35±2 | -459 | 100 | -137 | 74 | 91.6 |
| | 45±2 | -453 | 150 | -93 | 68 | 89.6 |
| | 55±2 | -466 | 260 | -87 | 60 | 88.2 |
| <i>P2</i> | 25±2 | -462 | 25 | -119 | 82 | 97.5 |
| | 35±2 | -467 | 45 | -100 | 72 | 96.2 |
| | 45±2 | -474 | 80 | -94 | 67 | 94.5 |
| | 55±2 | -477 | 160 | -86 | 60 | 92.7 |

It is clear that all curves exhibit Tafel behaviour and show a little different effect in the anodic and cathodic branches. It is seen also that the inhibition efficiency decreased slightly with temperature.

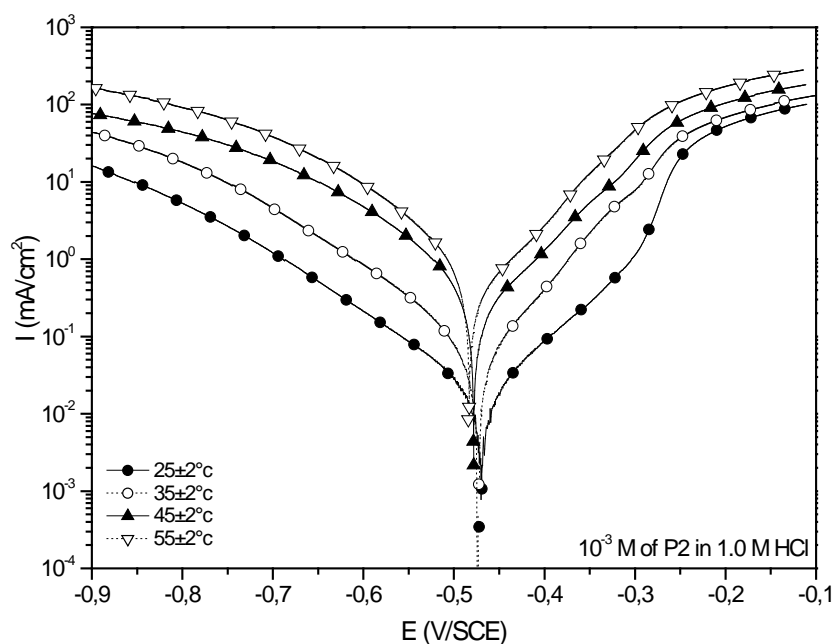


Fig. 10. Potentiodynamic polarization curves for carbon steel in 1.0 M HCl in the presence of 10^{-3} M of P2 at different temperatures between 25 ± 2 °C and 55 ± 2 °C

3.1.6. Thermodynamic parameters of Triphenylimidazole on carbon steel surface

Thermodynamic parameters are important to study the inhibitive mechanism. The thermodynamic functions for dissolution of mild steel in the absence and in the presence of various concentrations of Triphenylimidazole substituted compounds were obtained by applying the Arrhenius equation and the transition state equation [40–43].

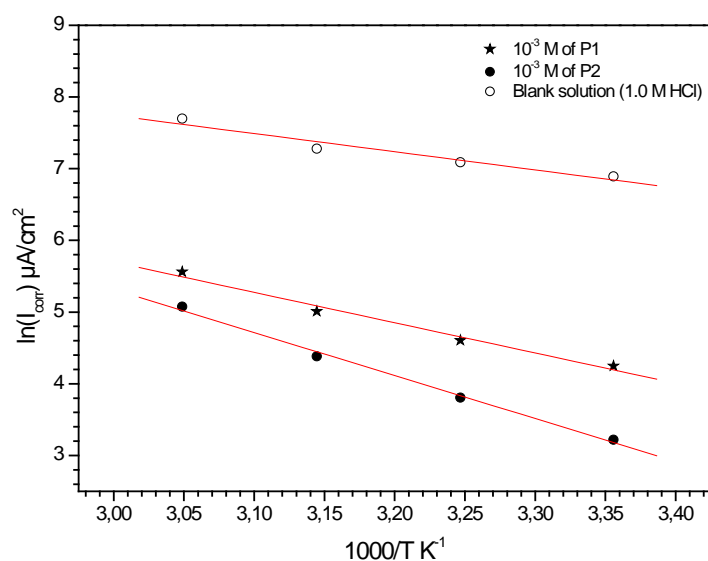


Fig. 11. Arrhenius plots of carbon steel in 1.0 M HCl without (a) and with (b) 10^{-3} M of Triphenylimidazole

However, the logarithm of corrosion rates ($\ln i_{\text{corr}}$) versus reciprocal of absolute temperature ($1/T$) for 1.0 M HCl without and with substituted quinolone was examined (Figure 12) using the Arrhenius equation:

$$\ln i_{\text{corr}} = -\frac{E_a}{RT} + \ln A \quad (9)$$

Where A is the Arrhenius pre-exponential constant, R is the universal gas constant, E_a is the apparent activation energy and T is the absolute temperature. The values obtained from the slope of the linear plots are shown in Table 7.

It is found that all the linear regression coefficients are close to 1, indicated that the corrosion of carbon steel in hydrochloric acid can be explained using the kinetic model. As observed from the Table 8, the E_a increased with Triphenylimidazole addition compared to the uninhibited solution (Blank solution).

Table 7. The values of activation parameters E_a , ΔH_a^* and ΔS_a^* for carbon steel in 1.0 M HCl and added of 10^{-3} M of the inhibitor's

| Compounds | E_a (KJ \times mol $^{-1}$) | ΔH_a^* (KJ \times mol $^{-1}$) | ΔS_a^* (J \times mol $^{-1}$ \times K $^{-1}$) |
|-------------------|----------------------------------|---|---|
| Blank solution | -2,53 | -2,22 | 8,59 |
| 10^{-3} M of P1 | -4,23 | -3,92 | 11,64 |
| 10^{-3} M of P2 | -5,99 | -5,68 | 16,55 |

Inspection of these data reveals that the thermodynamic parameters ΔH_{ads} and ΔS_{ads} of dissolution reaction of carbon steel in 1.0 M HCl in the presence of Triphenylimidazole are higher than in the absence of inhibitor. The positive sign of enthalpies reflect the endothermic nature of steel dissolution process meaning that dissolution of steel is difficult [44,45]. The increase in E_a in the presence of Triphenylimidazole may be interpreted as physical adsorption. Indeed, a higher energy barrier for the corrosion process in the presence of inhibitor's was associated with physical adsorption or weak chemical bonding between the inhibitors species and the carbon steel surface [31,32]. Szauer et al. have explained that the increase in E_a can be attributed to decrease in the inhibitor adsorption at metallic surface with the rise of temperature [33]. In this context, Singh et al. have considered that the increase in temperature caused an increase in the electron density at the adsorption centers, which improved the inhibition efficiency [42].

The other kinetic parameters such as enthalpy of adsorption (ΔH_a) and entropy of adsorption (ΔS_a) were obtained from transition state equation:

$$\ln \frac{i_{\text{corr}}}{T} = \ln \left(\frac{R}{Nh} \right) + \left(\frac{\Delta S_a}{R} \right) - \frac{\Delta H_a}{RT} \quad (10)$$

Where i_{corr} is the corrosion rate, h the Plank's constant and N is Avogadro's number, ΔH_a the enthalpy of activation and ΔS_a the entropy of activation.

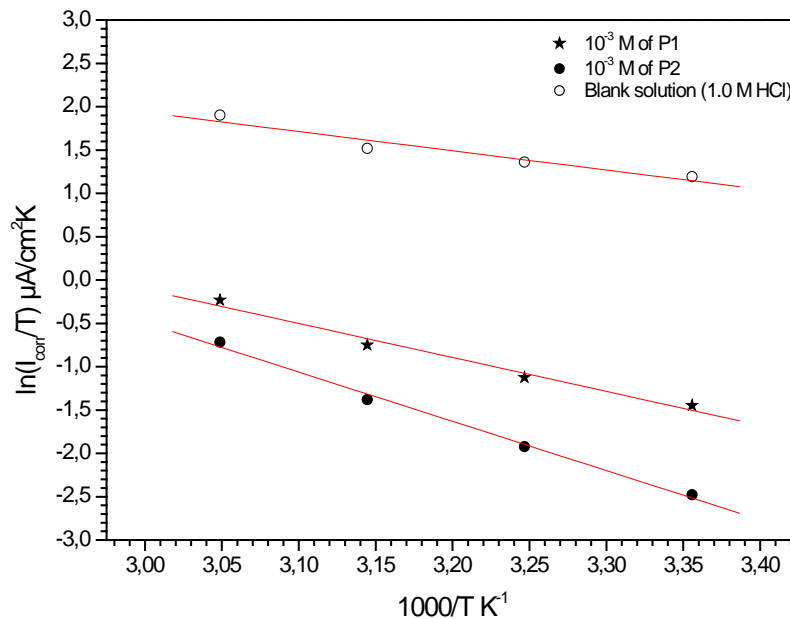


Fig. 12. Transition-state plots for mild steel corrosion rates $\ln j_{corr}$ versus $1/T$ in 1.0 M HCl without (a) and with (b) 10^{-3} M of Triphenylimidazole

Figure 12 shows the variation of $\ln(i_{corr}/T)$ function ($1/T$) as a straight line with a slope of $(-\Delta H_a/R)$ and the intersection with they-axis is $[\ln(R/Nh)+(\Delta S_a/R)]$. From these relationships, values of ΔS_a and ΔH_a can be determined. The activation parameters (ΔH_a and ΔS_a) which determined from the slopes of Arrhenius lines without and with inhibitors, are summarized in Table 5. It is seen that the ΔH_a value for dissolution reaction of mild steel in 1.0 M HCl in the presence of P2 is higher than that in the presence P1 and the free solution. In addition, the ΔH_a values in the presence P1 and P2 are lower than that in their absence .

However, the positive signs of ΔH_a values reveal the endothermic nature of the mild steel dissolution process suggesting that is difficult [46] with inhibitors. The same remarks were observed for the E_a values indicating that the corrosion process must involve a gaseous reaction, simply the hydrogen evolution reaction, associated with a decrease in the total reaction volume [47].

Additionally, Table 7 shows that the ΔS_a values increase with the presence of P2 compared to blank solution, which mean an increase in disorder during the transition from reactant to the activated complex during corrosion process. Also the ΔS_a values tend to more negative values as the P1 addition showing more ordered behaviour leading to increase inhibition efficiency.

3.6. Adsorption isotherm

It is generally assumed that the inhibitor adsorption onto the metal/solution interface is the first step in the mechanism of inhibition in aggressive media. Four types of adsorption may take place by heterocyclic molecules at the metal/solution interface: (1) electrostatic attraction between the charged metal and the charged molecules, (2) interaction of uncharged electrons pair in the molecule with the metal, (3) interaction of π electrons with the metal and (4) combination of (1) and (3) [42]. Chemical adsorption involves the share or charge transfer from the molecules onto the surface to form a coordinate type bond. Electron transfer is typical for transition metals having vacant low energy electron orbital. As for inhibitors, the electron transfer can be expected with compounds having relatively loosely bound electrons. A correlation between θ and inhibitor concentration C in the aqueous solution can be represented by the Langmuir adsorption isotherm [43,46]:

$$\theta = \frac{KC}{1+KC} \quad (11)$$

Rearranging this equation, it becomes:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (12)$$

where K represents the constant of adsorption reaction.

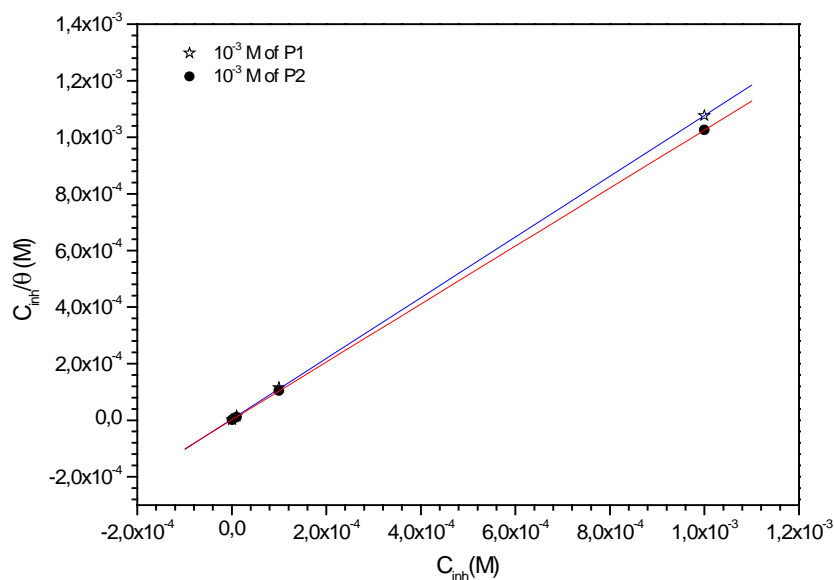


Fig. 14. Plot of the Langmuir adsorption isotherm of Triphenylimidazole on the carbon steel surface at 25 ± 2 °C

Figure 14 exemplifies the relation between C/θ and C at 25 ± 2 °C. It yields a straight line with slope close to unity. The strong correlation ($r^2=0.999$) for the Langmuir adsorption isotherm plot confirms the validity of this approach. Thus, we obtained the value of K for the inhibitors

used is $6.3 \times 10^{-5} \text{ L.mol}^{-1}$ and $4.2 \times 10^{-4} \text{ L.mol}^{-1}$ respectively for P1 and P2. The adsorptive equilibrium constant K is in relation with the standard free energy of adsorption [43,47].

$$K = \frac{1}{55.55} \exp\left(-\frac{\Delta G_{ads}}{RT}\right) \quad (13)$$

Where R is the universal gas constant, T is the thermodynamic temperature and value of 55.55 is the water concentration in the solution (mol.L^{-1}).

We found that all Triphenylimidazole substituted compounds show a good linear fit proving that the adsorption of these compounds from 1.0 M HCl solution on the carbon steel surface obeys the Langmuir adsorption isotherm. It is well known that values of ΔG_{ads} of the order of 20 kJ/mol or lower indicate a physisorption, those of order of 40 kJ/mol or higher are associated with chemisorptions as a result of the sharing or transfer of electrons from organic molecules to the metal surface to form a co-ordinate [33,35,48]. The negative values of ΔG_{ads} indicated the spontaneous adsorption of inhibitor on surface of carbon steel.

3.8. Surface analysis by SEM

Scanning Electronic Microscopy (SEM) analysis was performed to investigate the surface morphology of the carbon steel after immersion in 1.0 M HCl in the absence and presence of 10^{-3} M of P1 and P2 exposed for 6 hr at $25 \pm 2 \text{ }^\circ\text{C}$, The SEM micrograph of the deteriorated specimen in the presence of 1.0 M HCl solution are shown in Fig. 15 (a).

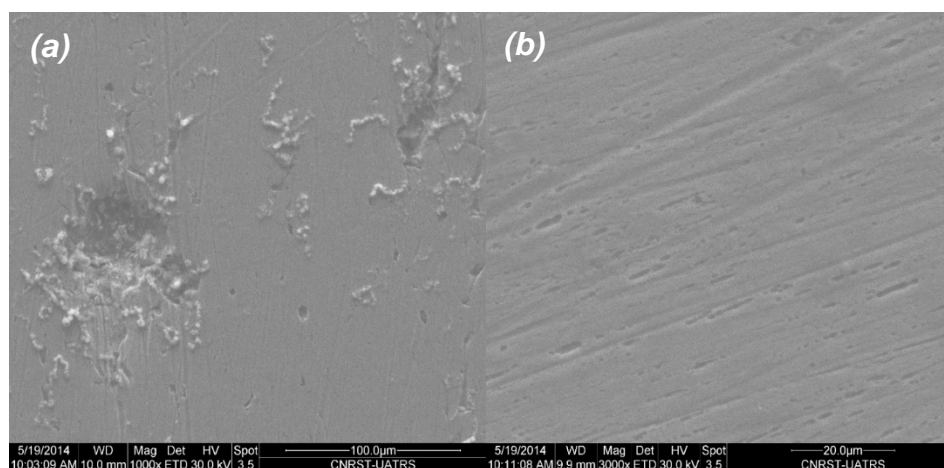


Fig. 15. Surface morphology of carbon steel after immersion for 6 h in 1.0 M HCl (a) without inhibitors and (b) with 10^{-3} M of P2

The faceting seen in this figures was a result of pits formed due to the exposure of carbon steel to the acid media. The influence of the P2 addition on the carbon steel in 1.0 M HCl solution is shown in Fig. 15 (b). The morphology shows a rough surface, characteristic of uniform corrosion of carbon steel in acid, that corrosion does not occur in presence of

inhibitor and hence corrosion was inhibited strongly when the inhibitor was present in the hydrochloric, and the surface layer is very rough. In contrast, in the presence of 10^{-3} M of P2, there is much less damage on the steel surface, which further confirm the inhibition action. Also, there is an adsorbed film adsorbed on carbon steel surface Fig. 15 (b). In accordance, it might be concluded that the adsorption film can efficiently inhibits the corrosion of carbon steel.

4. CONCLUSION

All the examined Triphenylimidazole substituted compounds are effective corrosion inhibitors for carbon steel in 1.0 M HCl solution. These compounds react as mixed type inhibitors. They act by adsorption mechanism where their inhibition depends on the concentration and the type of alkyl in their structures and the molecules with electron donating (-OH) substituents showed higher protection efficiency for the metal. In addition, the inhibition efficiency decreases slightly with temperature. So, it is found also that the order of this inhibition was confirmed by all techniques measurements. The adsorption of P1 and P2 obeys Langmuir adsorption isotherm. The adsorption process is a spontaneous and exothermic process accompanied by an increase of entropy. Potentiodynamic polarization curves reveals that Triphenylimidazole substituted compounds is a mixed-type but predominantly cathodic inhibitor. The results obtained from weight loss, impedance and polarization studies are in a good agreement.

REFERENCES

- [1] Y. El Kacimi, R. Tourir, M. Galai, R. A. Belakhmima, A. Zarrouk, K. Alaoui, M. Harcharras, H. El Kafssaoui, and M. Ebn Touhami, *J. Mater. Environ. Sci.* 7 (2016) 371.
- [2] M. HazwanHussin, M. Jain Kassim, N. N. Razali, N. H. Dahon, and D. Nasshorudin. *Arabian J. Chem.* (2011) 1878.
- [3] Y. Abbouda, A. Abourriche, T. Saffaj, M. Berrada, M. Charrouf, A. Bennamara, N. Al Himidi, and H. Hannache. *Mater. Chem. Physics.* 105 (2007) 1.
- [4] A. O. James, N. C. Oforika, and K. Abiola, *Int. J. Electrochem. Sci.* 2 (2007) 284.
- [5] E. E. Ebenso, *J. Chem. Res.* 6 (2001) 8.
- [6] M. Galai, M. El Gouri, O. Dagdag, Y. El Kacimi, A. El Harfi, and M. Ebn Touhami, *J. Chem. Pharm. Res.* 7 (2015) 712.
- [7] Y. Elkacimi, M. Achnin, Y. Aouine, M. Ebn Touhami, A. Alami, R. Tourir, M. Sfaira, D. Chebabe, A. Elachqar, and B. Hammouti, *Portugaliae Electrochim. Acta* 30 (2012) 53.
- [8] E. A. Noor, and A. H. Al-Moubaraki, *Int. J. Electrochem. Sci.* 3 (2008) 806.

- [9] K. Alaoui, Y. El Kacimi, M. Galai, K. Dahmani, R. Tourir, A. El Harfi, and M. Ebn Touhami, *Anal. Bioanal. Electrochem.* 8 (2016) 830.
- [10] Esmael Naderi, A. H. Jafari, M. Ehteshamzadeh, and M. G. Hosseini, *Mater. Chem. Phys.* 115 (2009) 852.
- [11] F. Bentiss, M. Lagrenee, M. Traisnel, and J. C. Hornez, *Corros. Sci.* 41 (1999) 789.
- [12] M. Galai, M. El Gouri, O. Dagdag, Y. El Kacimi, A. Elharfi, and M. Ebn Touhami, *J. Mater. Environ. Sci.* 7 (2016) 1562.
- [13] M. Ehteshamzade, T. Shahrabi, and M. G. Hosseini, *Appl. Surf. Sci.* 252 (2006) 2949.
- [14] M. Lebrini, F. Bentiss, H. Vezin, and M. Lagren´ee, *Corros. Sci.* 48 (2006) 1279.
- [15] S. A. Abd El-Maksoud, *Appl. Surf. Sci.* 206 (2003) 129.
- [16] H. H. Hassan, E. Abdelghani, and M. A. Amina. *Electrochim. Acta* 52 (2007) 6359.
- [17] S. Kertit, and B. Hammouti, *Appl. Surf. Sci.* 161 (1996) 59.
- [18] G. K. Gomma, *Mater. Chem. Phys.* 55 (1998) 241.
- [19] A. Chetouani, B. Hammouti, T. Benhadda, and M. Daoudi, *Appl. Surf. Sci.* 249 (2005) 375.
- [20] K. F. Khaled, *Mater. Chem. Phys.* 112 (2008) 290.
- [21] A. Chetouani, A. Aounti, B. Hammouti, N. Benchat, T. Benhadda, and S. Kertit, *Corros. Sci.* 45 (2003) 1675.
- [22] M. H. Wahdan, *Mater. Chem. Phys.* 49 (1997) 135.
- [23] D. Wahyuningrum, Synthesis of Imidazole Derivatives and Determination of Corrosion Inhibition Activity on Carbon Steel Surface, in Program Studi Kimia - FMIPA. 2008, Institut Teknologi Bandung: Bandung.
- [24] S. Das Sharma, P. Hazarika, and D. Konwar, *Tetrahedron Lett.* 49 (2008) 2216.
- [25] T. Prisinano, H. Law, M. Dukat, A. Slassi, N. MaClean, L. Demchyshyn, and R. A. Glennon, *Bioorg. Med. Chem.* 9 (2001) 613.
- [26] S. Bhor, G. Anilkumar, M. K. Tse, M. Klawonn, C. Döbler, B. Bitterlich, A. Grotevendt, and M. Beller, *Org. Lett.* 7 (2005) 3393.
- [27] J. G. Lambardino, and E. H. Wiseman, *J. Med. Chem.* 17 (1974) 1182.
- [28] A. K. Takle, M. J. B. Brown, S. Davies, D. K. Dean, G. Francis, A. Gaiba, A. W. Hird, F. D. King, P. J. Lovell, A. Naylor, A. D. Reith, J. G. Steadman, and D. M. Wilson, *Bioorg. Med. Chem. Lett.* 16 (2006) 378.
- [29] H. Veisi, A. Khazaei, L. Heshmati, and S. Hemmati, *Bull. Korean Chem. Soc.* 33 (2012) 1231.
- [30] ASTM G-81, Annual Book of ASTM Standards (1995).
- [31] M. Stern, and A. L. Geary, *J. Electrochem. Soc.* 104 (1957) 56.
- [32] M. S. Abdelaal, S. Radwan, and A. El Saied, *Br. Corros. J.* 18 (1983) 82.
- [33] W. Peters, *Chemotherapy and Drug Resistance in Malaria*, Academic Press London, New York (1970).

- [34] M. Sato, T. Motomura, and H. Aramaki, *J. Med. Chem.* 49 (2006) 1506.
- [35] I. B. Obot, and N. O. Obi-Egbedi, *Mater. Chem. Phys.* 122 (2010) 325.
- [36] A. A. Watson, G. W. J. Fleet, N. Asano, R. J. Molyneux, and R. J. Nugh, *Phytochemistry* 56 (2001) 265.
- [37] G. J. Atwell, B. C. Baguley, and W. A. Denny, *J. Med. Chem.* 32 (1989) 396.
- [38] Y. Xia, Z. Y. Yang, P. Xia, K. F. Bastow, Y. Tachibani, S. C. Kuo, E. Hamel, T. Hackl, and K. H. Lee, *J. Med. Chem.* 41 (1998) 1155.
- [39] H. F. Finley, and N. Hackerman, *J. Electrochem. Soc.* 107 (1960) 259.
- [40] I. El Ouali, B. Hammouti, A. Aouniti, Y. Ramli, M. Azougagh, E. M. Essassi, and M. Bouachrine *J. Mater. Environ. Sci.* 1 (2010) 1
- [41] G. Gunasekaran, and L. R. Chauhan, *Electrochim. Acta* 49 (2004) 4387.
- [42] ASTM G-81, *Annual Book of ASTM Standards* (1995).
- [43] M. Stern, and A. L. Geary, *J. Electrochem. Soc.* 104 (1957) 56.
- [44] Y. Tang, F. Zhang, S. Huc, Z. Cao, Z. Wu, and W. Jing, *Corros. Sci.* 74 (2013) 271.
- [45] A. Methal, A. Koulou, M. El Bakri, M. Ebn Touhami, M. Galai, M. Lakhrissi, R. Tourir, and S. Bakkali, *J. Pure Appl. Sci.* 1 (2015) 46.
- [46] G. J. Brug, A. L. G. Van Den Eeden, M. Sluyters-Rehbach, and J. H. Sluyters, *J. Electroanal. Chem.* 176 (1984) 275.
- [47] M. Moradi, J. Duan, and X. Du, *Corros. Sci.* 69 (2013) 338.
- [48] K. Alaoui, Y. El Kacimi, M. Galai, R. Tourir, K. Dahmani, A. Harfi, and M. Ebn Touhami. *J. Mater. Environ. Sci.* 7 (2016) 2389.