

Corrosion inhibition studies for mild steel in 5.0 M HCl by substituted phenyltetrazole

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Abstract The inhibition efficiency of three substituted phenyltetrazole compounds, namely 5-(4-chlorophenyl)-1*H*-tetrazole (Cl-PT), 5-(4-methoxyphenyl)-1*H*-tetrazole (MO-PT), and 5-phenyl-1*H*-tetrazole (PT), for mild steel corrosion in 5.0 M HCl solution was investigated using weight loss measurements and electrochemical study. It is showed that these compounds are good inhibitors for mild steel corrosion in 5.0 M HCl solution which act as cathodic type inhibitors. So, the inhibition efficiency was increased with inhibitor concentration in the order of Cl-PT > MO-PT > PT which depended on their molecular structures. It is found also that these compounds take its performance at different temperatures range from 298 to 328 K. In addition, the thermodynamic adsorption parameters at different concentrations were investigated and discussed. Finally, it is seen that the inhibition efficiency of the studied compounds increased with immersion time to reach a maximum at 12 h.

Keywords Corrosion and inhibition · Substituted phenyltetrazole · Mild steel · 5.0 M HCl · Electrochemical measurements

Introduction

Iron and its alloys used in industrial sectors became a great challenge for corrosion engineers or scientists (El Kacimi et al. 2016). So, to remove the scale and other products from the metal working, cleaning of boilers and heat exchangers, the acid solutions are commonly used. In these cases the metals were damaged by corrosion phenomena. Thus, to minimize this problem, many inhibitors are used (HazwanHussin et al. 2011; Abboud et al. 2007; James et al. 2007). In addition, organic compounds have many advantages such as high inhibition efficiency (Ebenso 2001; Elkacimi et al. 2012), low price, and easy production. Today, the development of new corrosion inhibitors based on organic compounds having multiple bonds, nitrogen and/or sulfur atoms in their structures have been employed. Among these, several triazoles (Noor and Al-Moubaraki 2008; Abouchane et al. 2015; El Bakri et al. 2008), tetrazole (Li et al. 2007; Hmimou et al. 2012), pyrazoles (Elkacimi et al. 2012), imidazoles (Zerga et al. 2010; Scendo and Hepel, 2007; Lamkaddem et al. 2007), pyridazines (Larabi et al. 2006; Benbouya et al. 2014), quinoxaline (Tazouti et al. 2016; Adardour et al. 2015), benzamide derivatives (Adardour et al. 2013), quinolone (El Faydy et al. 2016), etc. have been used as corrosion inhibitors for metals in corrosive medium. The choice of these products was based on their greater adsorption at the metallic (Adardour et al. 2013).

The aim of this work is to investigate the influence of three substituted phenyltetrazole for corrosion inhibitor of

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mild steel in 5.0 M HCl solution using weight loss and electrochemical measurements. The effect of temperature and immersion time was also studied.

Experimental details

The used steel specimens have a rectangular form 2.5 cm × 2.0 cm × 0.05 cm and have the following chemical composition (wt%) : C, 0.041; Mn, 0.171; Si, 0.150; P, 0.021; S, 0.005; Al, 0.043; Ca, 0.002; Mo, 0.009; Cu, 0.181; Ni, 0.074; Sn, 0.025; Nb, 0.001; Fe, balance. The specimen's surface was polished with emery paper, rinsed with distilled water, degreased with ethanol, and dried at hot air. The immersion time for weight loss was 24 h at 298 ± 1 K. After immersion period, the specimens were cleaned according to ASTM G-81 and reweighed to 10⁻⁴ g for determining corrosion rate (ASTM G 81-97a 2007). The aggressive medium of 5.0 M HCl was prepared by dilution of analytical grade 37% HCl with distilled water. The examined inhibitors are 5-phenyl-1*H*-tetrazole (PT), 5-(4-chlorophenyl)-1*H*-tetrazole (Cl-PT) and 5-(4-methoxyphenyl)-1*H*-tetrazole (MO-PT) where their molecular formulas are indicated in Table 1. The inhibition efficiency, η_w (%), was calculated using following equation:

$$\eta_w \% = \frac{\omega_{\text{corr}}^0 - \omega_{\text{corr}}}{\omega_{\text{corr}}^0} \times 100, \quad (1)$$

where ω_{corr}^0 and ω_{corr} are the corrosion rates without and with inhibitors, respectively.

For electrochemical measurements, the electrolysis cell closed by a cap with five apertures. The working electrode was pressure-fitted into a polytetrafluoroethylene holder (PTFE) exposing only 1 cm² of area to the aggressive solution. Pt 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, with a scan rate of 1 mV/s after 1 h of immersion time until reaching steady state. The test solution was thermostatically controlled at 298 ± 1 K in air atmosphere without bubbling. To evaluate corrosion kinetic parameters, a fitting by Stern-Geary equation was used (Stern and Geary 1957). The corrosion inhibition efficiency was evaluated from the corrosion current densities values using the relationship (2):

$$\eta_{\text{PP}} = \frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0} \times 100, \quad (2)$$

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

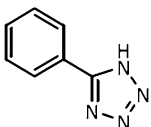
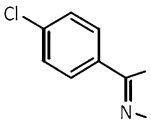
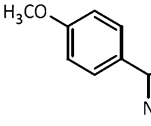
Finally, the electrochemical impedance spectroscopy measurements were carried out using a transfer function analyzer, with a small amplitude a.c. signal (10 mV rms), over a frequency domain from 100 kHz to 100 mHz with five points per decade. The results were then analyzed in terms of an equivalent electrical circuit using EC-Lab software. The inhibition efficiency, η_{EIS} , was calculated using the following Eq. (3):

$$\eta_{\text{EIS}} \% = \frac{R_p^0 - R_p}{R_p^0} \times 100, \quad (3)$$

where R_p^0 and R_p are the polarization resistance values without and with inhibitors, respectively.

To ensure reproducibility, all experiments were repeated three times where the evaluated inaccuracy did not exceed 10%.

Table 1 Weight loss data of mild steel without and with different concentration of PT, Cl-PT and MO-PT at 298 ± 1 K after 24 h of immersion in 5.0 M of HCl

Compounds	Conc. (M)	ω_{corr} (mg cm ⁻² h ⁻¹)	η_w (%)
Blank solution	00	35.088	–
PT 	10 ⁻⁴	13.9913	60.13
	5 × 10 ⁻⁴	10.6400	69.68
	10 ⁻³	8.7150	75.16
Cl-PT 	10 ⁻⁴	6.9700	80.14
	5 × 10 ⁻⁴	4.7300	86.52
	10 ⁻³	2.9990	91.45
MO-PT 	10 ⁻⁴	10.4800	70.13
	5 × 10 ⁻⁴	9.2900	73.52
	10 ⁻³	8.1150	76.87

Results and discussion

Weight loss studies

The corrosion rate values (ω_{corr}) of mild steel in 5.0 M HCl at different concentrations of substituted phenyltetrazole are presented in Table 1. It is noted that phenyltetrazole compounds act as good corrosion inhibitors and their inhibition increase with their concentrations and follow the order: Cl-PT > MO-PT > PT. This order can be explained by the rise of the effective electron density at the functional group of inhibitors (Elkacimi et al. 2012). So, the compounds have aromatic or heterocyclic ring, the effective electron density at the functional group can be change by the introduction of different substituent's in the ring causing the variations on their molecular structure; therefore a change in their corrosion inhibition efficiencies.

Potentiodynamic polarization studies

The potentiodynamic polarization behavior of mild steel in 5.0 M HCl without and with different concentrations of all substituted phenyltetrazole compounds are shown in Fig. 1a–c. Their electrochemical data are given in Table 2. It is known that the electrochemical reactions of the mild steel in acidic medium, in the absence of inhibitors, is the anodic dissolution reaction of iron and cathodic reactions related to the proton reduction:



However, in the presence of inhibitors, a shift of the corrosion potential E_{corr} toward more negative values for all compounds was observed. So, a great definite change on the corrosion potential (E_{corr}) was observed. According to Riggs (1973), if the displacement in E (1) is $>85 \text{ mV}/E_{\text{corr}}$, the inhibitor can be seen as a cathodic or anodic type, (2) if displacement in E is $<85 \text{ mV}/E_{\text{corr}}$, the inhibitor can be seen as mixed type. In our study, the displacement in the case of all products was more than $85 \text{ mV}/E_{\text{corr}}$, which indicated that PT, Cl-PT, and MO-PT were the cathodic type inhibitors.

In addition, it is clear that the current density decreases with increasing of the substituted phenyltetrazole concentration; this indicates that these compounds are adsorbed on the metal surface and hence inhibition occurs. The potentiodynamic polarization curves (Fig. 1a–c) show that these inhibitors have an effect on both, the cathodic and anodic slopes (β_c and β_a) and suppressed both cathodic and anodic processes. This indicated a modification of the mechanism of cathodic hydrogen evolution [Eq. (5)] as well as anodic dissolution of iron [Eq. (4)], which suggest that the

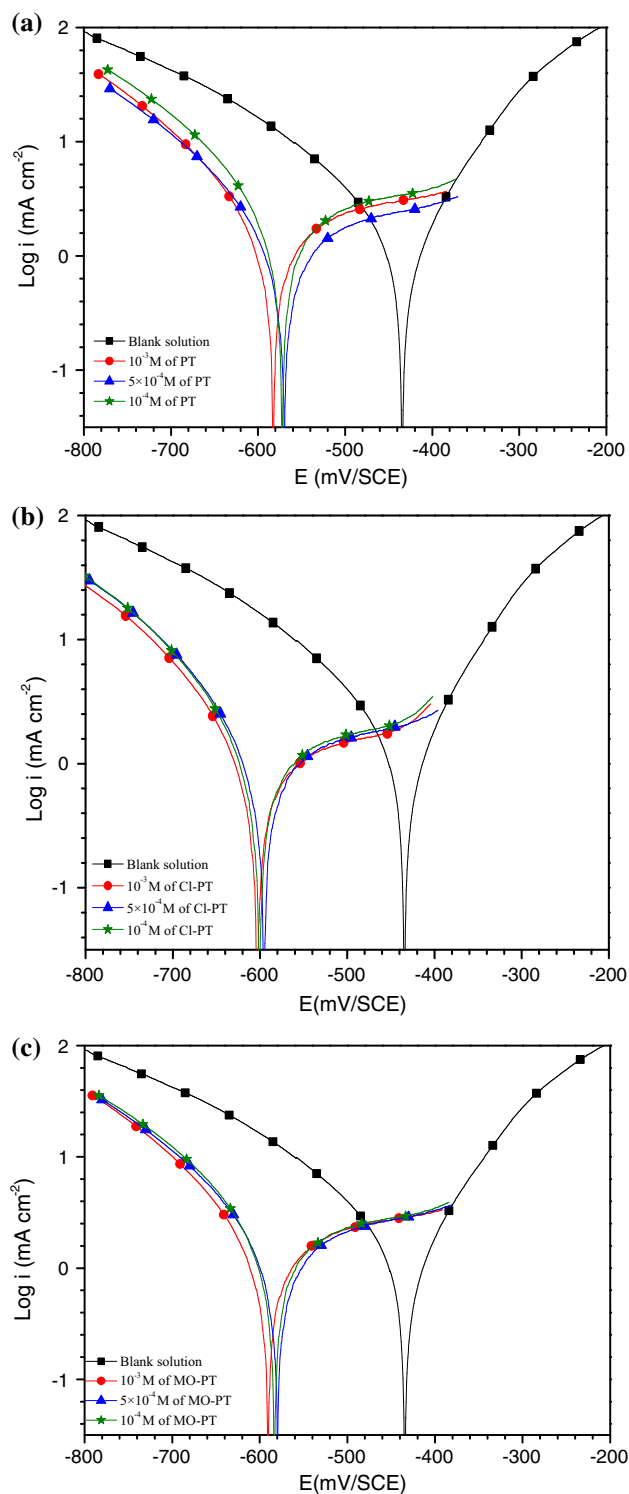


Fig. 1 Potentiodynamic polarization curves for mild steel in 5.0 M HCl containing different concentration of **a** PT, **b** Cl-PT and **c** MO-PT

substituted phenyltetrazole powerfully inhibit the corrosion process of mild steel, and their ability as corrosion inhibitors are enhanced as their concentrations are increased.

Table 2 Potentiodynamic electrochemical parameters obtained for mild steel in 5.0 M HCl containing different concentrations of substituted phenyltetrazole compounds

Compounds	Conc. (M)	E_{corr} (mV/SCE)	i_{corr} (mA cm ⁻²)	β_a (mV dec ⁻¹)	$-\beta_c$ (mV dec ⁻¹)	η_{EIS} (%)
Blank solution	00	-434.10	1.3699	144.00	95.00	-
PT	10 ⁻⁴	-572.40	0.4461	105.00	63.00	67.44
	5 × 10 ⁻⁴	-573.80	0.4071	85.70	58.00	70.28
	10 ⁻³	-595.00	0.3718	47.00	40.00	72.86
Cl-PT	10 ⁻⁴	-594.20	0.2149	40.00	36.00	84.31
	5 × 10 ⁻⁴	-601.40	0.1470	27.00	22.00	89.27
	10 ⁻³	-603.70	0.1203	24.00	22.00	91.21
MO-PT	10 ⁻⁴	-579.70	0.3459	56.20	43.00	74.75
	5 × 10 ⁻⁴	-569.30	0.2890	43.00	36.00	78.90
	10 ⁻³	-590.40	0.2601	46.70	37.40	81.01

The suppression of cathodic process can be due to the covering of the mild steel surface with monolayer due to the adsorbed inhibitor molecules. It can also be seen from Table 2, that the values of anodic Tafel slope β_a decrease in the presence of all compounds. This observation may be ascribed to changes in the charge transfer coefficient α_a for the anodic dissolution of Fe by virtue of the presence of an additional energy barrier due to the presence of adsorbed inhibitors (Abboud et al. 2007). Finally, it is seen also that all compounds bring down (i_{corr}) value at all concentrations and the minimum values was obtained at 10⁻³ M and the η_{PP} followed the order: Cl-PT > MO-PT > PT such as found by the weight loss measurements.

Electrochemical impedance spectroscopy (EIS)

Figure 2a–c shows the Nyquist plots obtained for mild steel in 5.0 M HCl without and with different concentrations of substituted phenyltetrazole compounds at the open circuit potential. It is apparent that the obtained spectra were composed of one capacitive loop attributed to the transfer charge, in which its diameter was significantly increased after inhibitors' addition to reach a maximum at 10⁻³ M of all compounds.

The slightly depressed nature of the semi-circles in Nyquist diagrams is characteristic for the solid electrode which has the center below the x -axis. Impedance spectroscopy studies on the double-layer capacitance at solid electrodes usually show deviations from ideal behavior. The dispersion has been attributed to roughness and other inhomogeneity of the solid electrode and also anion adsorption. The anomalous capacitance dispersion can be represented by a so-called constant phase element, CPE (Conway 1991), and the impedance of the CPE (Z_{CPE}) can be expressed as follows (Halim et al. 2012; Ashassi-Sorkhabi and Asghari 2010):

$$Z_{\text{CPE}} = \frac{1}{Y_0(j\omega)^n}, \quad (6)$$

where Y_0 is the CPE constant, n is the CPE exponent. $J^2 = -1$, and ω is the angular frequency. Depending on the value of n , CPE can represent a resistance. n is a measure of non-ideality of the capacitor and has a value ranging from -1 to 1 (Negm et al. 2011). The double-layer charge transfer, C_{dl} , can be calculated as follows:

$$C_{\text{dl}} = (Y_0 R_{\text{ct}}^{1-n})^{\frac{1}{n}}. \quad (7)$$

The physical description of the corrosion process of mild steel in 5.0 M HCl in the presence of different concentration of inhibitors was analyzed by modeling the metal/solution interface to an equivalent electrical circuit indicated in the insert in Fig. 2a–c. The elements of the circuit can be named as follows— R_s is the solution resistance, R_{ct} is the charge transfer resistance, and CPE_{dl} is the constant phase element of the double layer. The data obtained by fitting the EIS results were summarized in Table 3.

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 mild steel corrosion in 5.0 M HCl was controlled by a charge transfer process and the corrosion inhibition occurs by the adsorption of the substituted phenyltetrazole compounds on mild steel surface. However, the decrease in the C_{dl} values, which can result from a decrease in local dielectric constant and/or an increase in current density, the thickness of the electrical double layer, suggested by adsorption of the phenyltetrazole molecules at the metal/solution interface (Bentiss et al. 2000; Abdallah 2002). It is remarked also that the n_{dl} values increase with increasing of the inhibitors concentrations. This can be explained by the decrease in surface heterogeneity as a result of the phenyltetrazole molecules adsorption on the mild steel

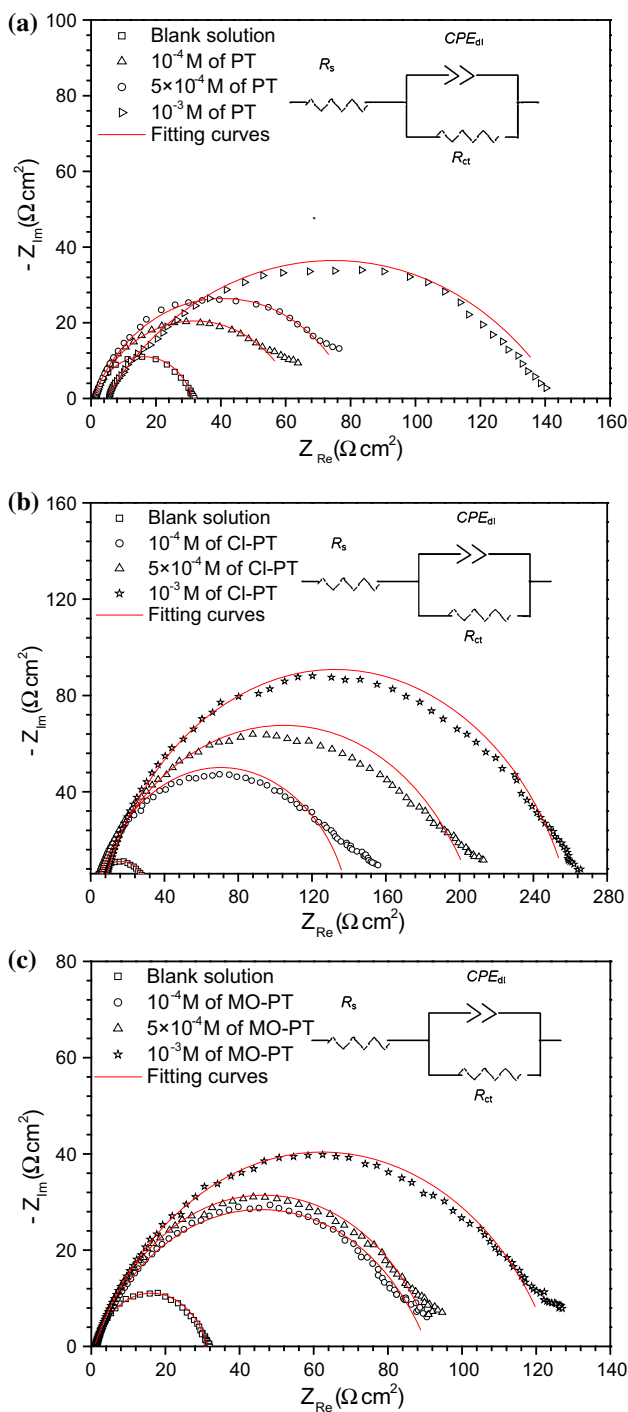


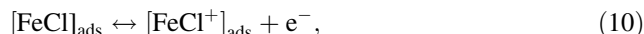
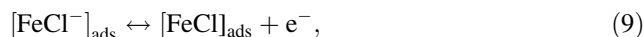
Fig. 2 Nyquist plots for mild steel in 5.0 M HCl at open circuit potential in the absence and presence of different concentrations of **a** PT, **b** Cl-PT and **c** MO-PT

surface. The same result was found by other authors, and they explained by the molecule adsorption of inhibitors via N and S atoms in the inhibitor molecules (Finšgar and Merl 2014; El Bakri et al. 2016).

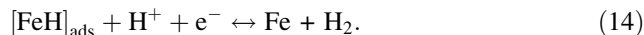
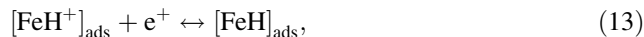
On the other hand, it is observed that the electrolyte solution increased with the inhibitors' addition. This can be explained by the protonation of the inhibitor molecules decreasing therefore the concentration of the H^+ ions in the solution. It is noted also that the inhibition efficiency follows the order: Cl-PT > PT > MO-PT, which is in a good agreement with results obtained from weight loss and potentiodynamic polarization measurements.

On the other hand, the effectiveness of organic compounds mainly depends on their size and their active centers (Ateya et al. 1976). The best performance of compound Cl-PT as corrosion inhibitors over compound MO-PT and PT may be attributed to the presence of $-Cl$ group in compound Cl-PT. The nucleophilic (electron releasing) character of $-Cl$ group is highest than the electrophonic (electron withdrawing). So, the lesser value of inhibition efficiency for PT and MO-PT as compared to compound Cl-PT can be attributed to the lower electron densities around the chemisorption center. Cl-PT can produce protonated species in HCl by the reaction of the amino group with HCl. This ammonium substituent may reduce the electronic density on the substituted phenyltetrazole compounds. The same results were observed by other authors (Elkacimi et al. 2012).

However, according to Trethewey and Chamberlain (1995), at a high concentration, anions present in the solution may either become inhibitive or act in such a way as to plug any pores in a passive film. The mechanism of the anodic dissolution of mild steel in HCl is (Behpour et al. 2008):



The mechanism for cathodic hydrogen evolution is (Solmaz 2010):



The mild steel surface is positively charged if the mechanism from Eq. (18) is utilized. In this case, it would be difficult for the protonated of the phenyltetrazole derivative molecules to approach the positively charged mild steel surface because of electrostatic repulsion. The presence of Cl^- ions which are adsorbed on the mild steel surface and thus facilitates the approach of the protonated phenyltetrazole derivatives molecules on the metal surface (EL-Gaber et al. 2008).

Table 3 Corrosion parameters obtained by impedance measurements for mild steel in 5.0 M HCl at various concentrations of substituted phenyltetrazole compounds

Inhibitors	Conc. (M)	R_s (Ω cm ²)	R_{ct} (Ω cm ²)	C_{dl} (μ F cm ⁻²)	n_{dl}	$\eta_{EIS}/\%$
Blank solution	00	1.25	30.27	142.00	0.63	–
PT	10 ⁻⁴	1.30	89.91	92.79	0.72	66.33
	5 × 10 ⁻⁴	1.50	91.08	108.8	0.74	66.76
	10 ⁻³	5.44	123.2	116.7	0.77	75.43
	10 ⁻⁴	2.79	136.20	70.62	0.75	77.77
Cl-PT	10 ⁻⁴	2.79	136.20	70.62	0.75	77.77
	5 × 10 ⁻⁴	4.16	203.90	33.17	0.79	85.15
	10 ⁻³	7.62	252.10	29.11	0.81	87.99
	10 ⁻⁴	1.25	62.42	106.4	0.74	48.49
MO-PT	10 ⁻⁴	1.25	62.42	106.4	0.74	48.49
	5 × 10 ⁻⁴	1.26	79.78	95.54	0.75	62.06
	10 ⁻³	1.40	139.9	31.15	0.80	78.36

Table 4 Electrochemical and activation parameters and the corresponding inhibition efficiencies at various temperature of mild steel in 5.0 M HCl in absence and presence of 10⁻³ M of phenyltetrazole derivative

Compounds	T (K)	E_{corr} (mV/SCE)	i_{corr} (mA cm ⁻²)	η_{PP} (%)	E_a (kJ mol ⁻¹)	ΔH_a (kJ mol ⁻¹)	ΔS_a (J K ⁻¹ mol ⁻¹)
Blank solution	298	-434.10	1.3699	–			
	308	-454.00	2.5206	–	26.33	23.74	-162.34
	318	-459.47	3.1559	–			
	328	-462.00	3.7073	–			
PT	298	-580.00	0.3718	72.86			
	308	-590.59	0.4737	81.21	18.40	15.81	-200.67
	318	-589.40	0.6257	80.17			
	328	-580.63	0.7193	80.59			
Cl-PT	298	-603.70	0.1203	91.21			
	308	-596.40	0.3584	85.96	36.56	33.96	-147.09
	318	-589.40	0.4200	86.69			
	328	-584.64	0.5012	86.48			
MO-PT	298	-590.4	0.2601	81.01			
	308	-589.44	0.4714	81.30	14.70	12.10	-213.41
	318	-588.19	0.5152	83.68			
	328	-584.04	0.6119	83.49			

Effect of temperature

The effect temperature on the corrosion inhibition of mild steel 5.0 M HCl without and with inhibitors was studied in the temperature range 298–328 K. Table 4 shows the electrochemical parameters extracted from the potentiodynamic polarization curves of mild steel in 5.0 M HCl in the presence of 10⁻³ M of each substituted phenyltetrazole compounds. It is clear that the current density values increased and the inhibition efficiency of the studied compounds decreased slightly with increasing of temperature.

However, the logarithm of corrosion rates ($\text{Ln}i_{\text{corr}}$) versus reciprocal of absolute temperature ($1/T$) for 5.0 M HCl without and with substituted phenyltetrazole was examined (Fig. 3a) using the Arrhenius equation:

$$\text{Ln}i_{\text{corr}} = -\frac{E_a}{RT} + \text{Ln}A, \tag{15}$$

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 4.

It is found that all the linear regression coefficients are close to 1, indicated that the corrosion of mild steel in hydrochloric acid can be explained using the kinetic model. As observed from the Table 4, the E_a increased with Cl-PT addition and decreased in the case of PT and MO-PT addition compared to the uninhibited solution (Blank solution). The increase in E_a in the presence of Cl-PT may be interpreted as physical adsorption. Indeed, a higher energy barrier for the corrosion process in the presence of inhibitors was associated with physical adsorption or weak chemical bonding between

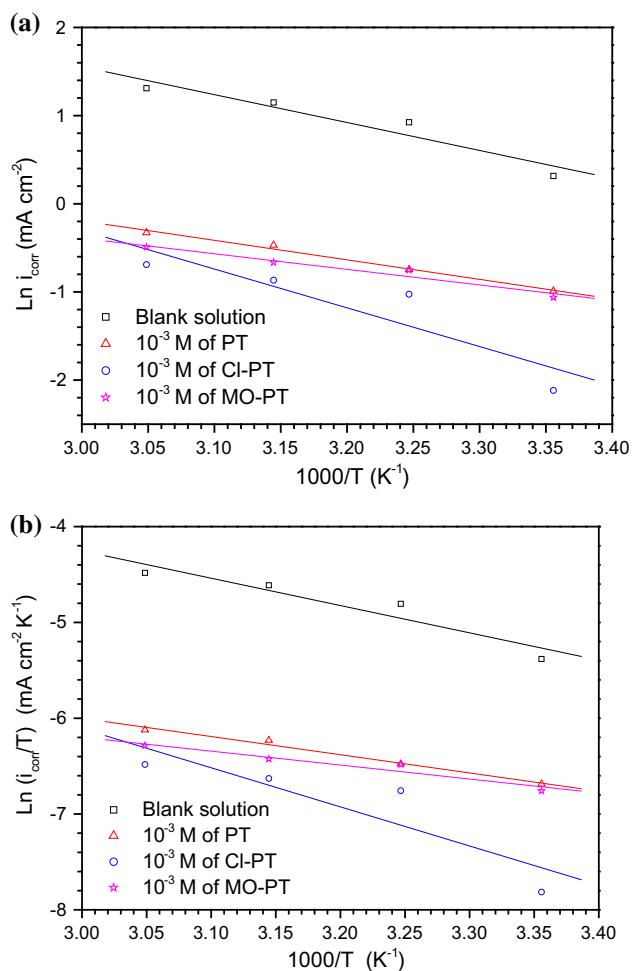


Fig. 3 a Arrhenius and b transition Arrhenius plots of mild steel in 5.0 M HCl without and with 10⁻³ M of different substituted phenyltetrazole

the inhibitor species and the mild steel surface (Popova et al. 2003; Elayyachy et al. 2005). 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 (Szauer and Brand 1981). Cl-PT is an organic base that easily protonates to give a cationic form in acid medium. The E_a value was greater than 20 kJ mol⁻¹ in both the presence and absence of inhibitor, which revealed that the entire process was controlled by the surface reaction (Herrag et al. 2010). So, the decrease of E_a in the case of PT and MO-PT probably was attributed to chemisorption of these inhibitors molecules on the mild steel surface (Venkatchalam et al. 1981; Sankarapavinasam et al. 1991). In this context, Singh et al. (1979) have considered that the increase in temperature caused an increase in the electron density at the adsorption centers, which improved the inhibition efficiency. The same results were obtained in the case of inhibition of galvanized steel in 3.0% NaCl (Azaroual et al. 2016).

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

$$\text{Ln} \frac{i_{\text{corr}}}{T} \ln \left(\frac{R}{Nh} \right) + \left(\frac{\Delta S_a}{R} \right) - \frac{\Delta H_a}{RT}, \quad (16)$$

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. Figure 3b shows the variation of $\text{Ln} (i_{\text{corr}}/T)$ function ($1/T$) as a straight line with a slope of $(-\Delta H_a/R)$ and the intersection with the y-axis is $[\text{Ln}(R/Nh) + (\Delta S_a/R)]$. 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 4. It is seen that the ΔH_a value for dissolution reaction of mild steel in 5.0 M HCl in the presence of Cl-PT is higher than that in the presence PT, MO-PT, and the free solution. In addition, the ΔH_a values in the presence PT and MO-PT are lower than that in their absence.

However, the positive values of ΔH_a for both corrosion processes without and with inhibitors reveal the endothermic nature of the mild steel dissolution process and indicate that the dissolution of the mild steel is difficult (Gerengi et al. 2009). The same remarks were observed for the E_a values indicating that the corrosion process must have involved a gaseous reaction, simply the hydrogen evolution reaction, associated with a decrease in the total reaction volume (Noor 2007).

Additionally, Table 4 shows that the ΔS_a values increase with the presence of Cl-PT compared to blank solution, which mean an increase in disorder during the transition from reactant to the activated complex during corrosion process (Singh and Quraishi 2011; Singh et al. 2011). Also the ΔS_a values tend to more negative values as the PT and MO-PT addition showing more ordered behavior leading to increased inhibition efficiency (Umoren et al. 2011).

Effect of immersion time

Figure 4 shows the obtained impedance spectra at different immersion time in 5.0 M HCl containing 10⁻³ M of PT, Cl-PT or MO-PT, respectively. It is noted that the Nyquist plot of mild steel in the presence of inhibitors for one hour of immersion contains a slightly depressed semi-circular shape and only one time constant was appeared indicating that the mild steel corrosion is mainly controlled by a charge transfer process. In this case, the equivalent electric circuit, Fig. 5a, with one time constant was used for describing the mild steel/solution interface in the presence of inhibitors at 298 K. The elements of the circuit can be named as— R_s is the solution resistance, R_{ct} is the charge

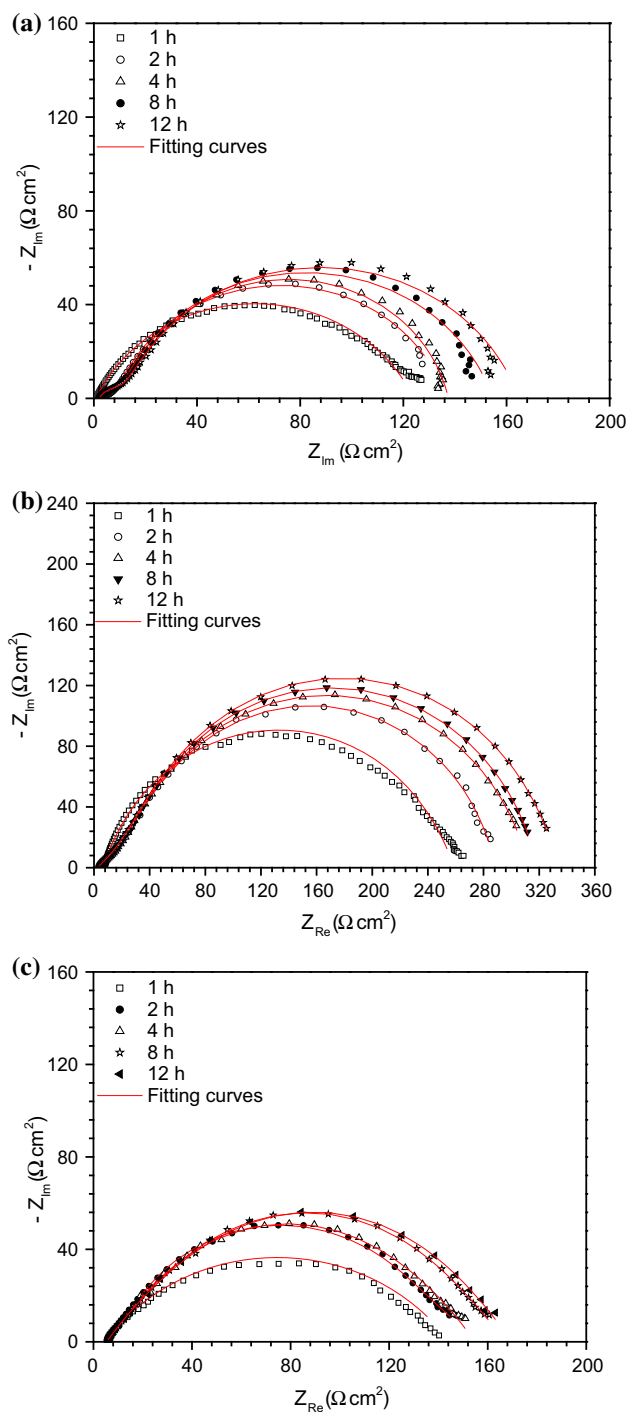


Fig. 4 Nyquist plots for mild steel in 5.0 M HCl at different immersion time at open circuit potential in the presence of 10^{-3} M of **a** PT, **b** Cl-PT and **c** MO-PT

transfer resistance, and CPE_{dl} is the constant phase element of the double layer such as indicated above.

So, for the immersion between 2 and 12 h, the equivalent circuit shown in Fig. 5b was used for fitting electrochemical responses of mild steel which have two loops in

the Nyquist plots. As shown in Fig. 5b an element was added into the circuit to define the mild steel/solution interface accurately. This added circuit element was presented as R_{ad} which reflects the film resistance of adsorbed inhibitor molecules, CPE_{ad} is the constant phase element of the film layers and CPE_{dl} is the constant phase element of the double layer in the equivalent circuit. The total resistance may be stated as $R_p = R_{ct} + R_{ad}$. The data obtained by fitting the EIS results were summarized in Table 5. It is noted that the values of both R_{ct} and R_{ad} increased with immersion time, and this effect are enhanced by increasing of immersion, demonstrating that a high-efficiency protective film is formed by the adsorption effect of these inhibitors on mild steel surface. Furthermore, the values of C_{ad} and C_{dl} , which can be expressed as Eqs. (6) and (7) below (Wang et al. 2014; Li et al. 2011), exhibit a decreasing trend with increasing of immersion time:

$$C_{dl} = \frac{\varepsilon_0 \times \varepsilon}{d} \times S, \quad (17)$$

$$C_{ad} = \frac{F^2 \times S}{4RT}, \quad (18)$$

where S is the surface area of mild steel electrode exposed to corrosive medium, d is the thickness of electric double layer, F is the Faraday's constant. ε_0 and ε are the permittivity of the air and the local dielectric constant, respectively. Therefore, the decrease of C_{ad} can be interpreted with the adsorption of these inhibitor molecules, which reduces the exposed electrode surface area at higher immersion time and inhibitor concentration and thus retards mild steel corrosion effectively.

Furthermore, water molecules on the mild steel surface are replaced gradually by inhibitor molecules at the metal/solution interface, leading to thicker electric double layer, lower local dielectric constant, and smaller exposed electrode surface. All these factors result in reduce of C_{dl} (Ma et al. 2001; Adardour et al. 2010). Furthermore, this decrease may be also caused by the fact that during immersion time, the adsorbed of the chlorides quantity increase on the metallic surface helping the adsorption of inhibitors (Touir et al. 2010; Belakhmima et al. 2015).

Consequently, inhibition efficiencies increase with immersion time and reach 80.78, 90.91, and 82.08% for PT, Cl-PT, and MO-PT at 12 h, respectively. The same order of the inhibition efficiency was followed: Cl-PT > PT > MO-PT.

Finally, it is shown that the n_{dl} values increase with inhibitors' addition and immersion time, which could be related to the decrease of the surface heterogeneity as a result of the inhibitor molecules adsorption on mild steel surface and forming a uniform inhibitive film (El Faydy et al. 2016).

Fig. 5 Electrical equivalent circuits used for modeling the metal/solution interface in the presence of each inhibitor at 10^{-3} M. **a** 1 h of immersion and **b** between 2 and 12 h of immersion

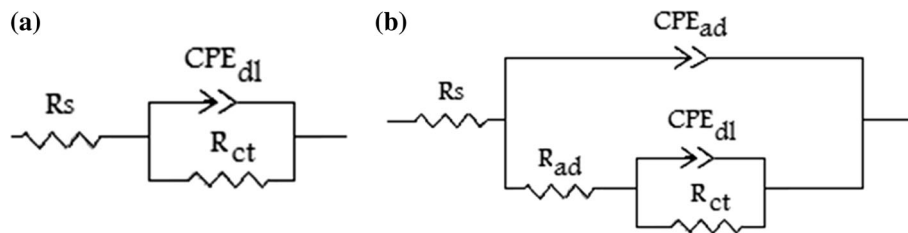


Table 5 Electrochemical parameters and the corresponding inhibition efficiencies at various immersion time of mild steel in 5.0 M HCl in the presence of 10^{-3} M of phenyltetrazole derivative

Time (h)	R_s (Ω cm ²)	R_{ad} (Ω cm ²)	C_{ad} (μ F/cm ²)	n_{ad}	R_{ct} (Ω cm ²)	C_{dl} (μ F/cm ²)	n_{dl}	R_p (Ω cm ²)	η_{EIS} %
10^{-3} M of PT									
1	5.44	–	–	–	123.20	116.70	0.77	123.20	75.43
2	5.53	6.25	45.92	0.81	127.50	89.59	0.78	133.75	77.37
4	3.51	8.25	34.35	0.81	130.01	51.82	0.79	138.26	78.11
8	6.50	8.41	26.05	0.82	144.50	50.44	0.83	152.92	80.21
12	11.85	9.1	24.29	0.87	148.35	47.99	0.84	157.47	80.78
10^{-3} M of Cl-PT									
1	7.62	–	–	–	252.10	29.11	0.81	252.10	87.99
2	4.13	27.26	42.05	0.85	256.90	28.95	0.56	284.16	89.35
4	5.53	28.98	40.17	0.87	278.40	28.50	0.48	307.38	90.15
8	4.13	30.78	24.7	0.87	288.20	22.47	0.57	318.98	90.51
12	4.14	49.36	12.04	0.88	283.50	13.13	0.45	332.86	90.91
10^{-3} M of MO-PT									
1	1.4	–	–	–	139.90	31.15	0.80	139.90	78.36
2	3.14	47.66	51.69	0.83	94.35	51.24	0.81	142.01	78.68
4	1.91	55.81	32.28	0.89	101.90	34.88	0.82	157.71	80.81
8	2.17	60.9	22.85	1	102.50	16.73	0.90	163.40	81.47
12	2.39	60.12	19.59	1	108.80	12.97	1	168.92	82.08

Conclusion

All the examined substituted phenyltetrazole compounds are effective corrosion inhibitors for mild steel in 5.0 M HCl solution. The potentiodynamic polarization curves indicated that these compounds act as cathodic type inhibitors and their inhibition efficiencies increased with their concentrations to reach a maximum at 10^{-3} M. It is found also that the mechanism of the hydrogen reduction and the iron dissolution reactions change by the inhibitors addition. They act by adsorption mechanism at the metallic surface and their inhibition depended on the nature of the alkyl presented in their structures and the Cl-PT compound is the best inhibitor. In addition, the inhibition efficiency decreased slightly with temperature and increased with immersion time to reach a maximum at 12 h. The thermodynamic study indicated that Cl-PT can be acted by physical adsorption whereas PT and MO-PT by chemisorptions at the metallic surface. The EIS measurements indicated that the plots were composed by one

capacitive loop in the case of 1 h of immersion time while they were composed by two loops for the immersion time range from 2 to 12 h. So, it is found also that the order of the inhibition efficiencies of the studied compounds were confirmed by all techniques' measurements.

On the other hand, it could be interesting also to study the action mode of these compounds using spectroscopy analysis techniques. It could provide information about the nature of adsorption of the substituted phenyltetrazole compounds on the metallic surface. It could be interesting also to study the effect of these compounds on the corrosion of another metal in another acidic medium such as H_2SO_4 and 1 M H_3PO_4 . This study confirmed the performance and the other application of the substituted phenyltetrazole compounds.

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Compliance with ethical standards

Conflict of interest All of the authors have declared no conflicts of interest.

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