Int. J. Electrochem. Sci., 7 **(2012)** 6313 - 6330

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

WL, I-E and EIS Studies on the Corrosion Behaviour of Mild Steel by 7-substituted 3-methylquinoxalin-2(1H)-ones and thiones in Hydrochloric Acid Medium

K. Benbouya[1], *B. Zerga*[2], *M. Sfaira*[2,*], *M. Taleb*[2], *M. Ebn Touhami*[1], *B. Hammouti*[3], *H. Benzeid*[4], *E.M. Essassi*[4]

[1] Laboratoire des Matériaux, Electrochimie et Environnement, Faculté des Sciences, Université Ibn Tofaîl, BP. 133 – 14000, Kénitra, Morocco
[2] Laboratoire d'Ingénierie des Matériaux, de Modélisation et d'Environnement, LIMME, Faculté des Sciences Dhar El Mahraz, Université Sidi Mohammed Ben Abdellah, USMBA, BP 1796 – 30000, Atlas – Fès, Morocco
[3] LCAE-URAC18, Faculté des Sciences, Université Mohammed Premier, BP 717 – 60000, Oujda, Morocco
[4] Laboratoire de Chimie Organique Hétérocyclique, pôle de compétences Pharmacochimie Faculté des sciences de Rabat, Université Mohammed V
[*]E-mail: msfaira@yahoo.com

Received: 29 May 2012 / *Accepted:* 18 June 2012 / *Published:* 1 July 2012

The present study examines the use of some 7-R-3-methylquinoxalin-2(1H)-ones and thiones, namely 3-methylquinoxalin-2(1H)-one (Q=O), 3-methylquinoxalin-2(1H)-thione (Q=S), 7-chloro-3-methylquinoxalin-2(1H)-one (Cl-Q=O) and 7-chloro-3-methylquinoxalin-2(1H)-thione (Cl-Q=S) for corrosion and dissolution protection of mild steel in 1 M HCl. The inhibiting efficiency of the different inhibitors under study is evaluated by means of weight loss and electrochemical techniques (potentiodynamic curves and impedance measurements). The experimental results reveal that Q=S > Cl-Q=S > Q=O > Cl-Q=O. The variation in inhibiting efficiency mainly depends on the type and nature of the chlorine group and the substitution of an atom of oxygen by a sulphur atom. Polarization curves exhibit that these quinoxaline derivatives are predominately cathodic type inhibitors and mixed-type in the case of Q=S in molar hydrochloric acid. The inhibiting efficiency increases with the quinoxaline derivatives and reaches the maximum value of ca. 90 % in the case of Q=S at 10^{-3} M. The results obtained from weight loss and electrochemical studies are in reasonable good agreement and follow the same trend. The adsorption of quinoxaline derivatives on the mild steel obeys to the Langmuir isotherm model.

Keywords: Quinoxaline derivatives; adsorption; 1 M HCl; Mild steel; Langmuir isotherm

1. INTRODUCTION

The damages caused by corrosion generate not only high costs for inspection, repairing and replacement, but in addition these constitute a public risk. In order to fight against this environmental consequence, several approaches have been designed to protect metallic installations in industries. However, one of the most effective and preferred option involves the use of inhibitors [1]. Most well-known acid inhibitors are organic substances, which is one of the most effective alternatives for the protection of metallic structures against corrosion in acid environments [2]. Thus the necessity of developing novel substances those behave like corrosion inhibitors.

In general, the organic compounds have demonstrated a great effectiveness in inhibiting the watery corrosion of many metals and alloys. It has been demonstrated that the compounds that have nitrogen and sulphur in their structure provide a greater inhibition than those containing only one of the atoms at a time, being this property attributable to its molecular structure [3]. These molecules may adsorb on metallic surfaces and then slow down the cathodic reaction as well as the anodic process of metal dissolution. Such effect is obtained by forming a barrier of diffusion or by means of the blockade of the reaction sites. Previously, some work has been done in our laboratory on N-heterocyclic inhibitors on mild steel in acid media like pyridazine [4-6], tripodal bipyrazol [7], tetrazol [8], pyridine-pyrazol [9] and have exhibited good inhibitory effect in hydrochloric acid. Notwithstanding several structural similarities with some of the above mentioned compounds, the derivatives of quinoxaline have scarcely been studied as mild steel corrosion inhibitors [10-12].

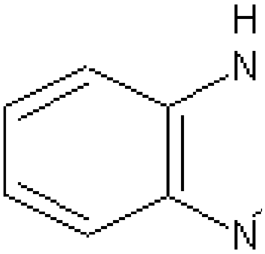
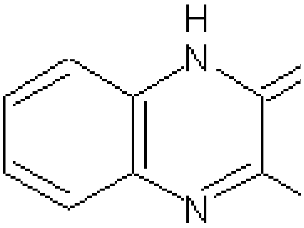
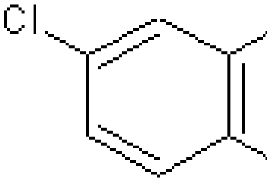
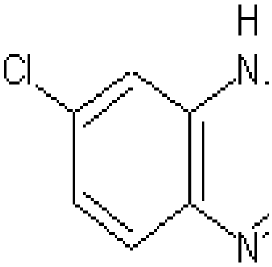
The present study was undertaken to investigate the mild steel corrosion inhibition in molar hydrochloric acid by some newly quinoxaline derivatives and to follow the effect of the substitution of an oxygen atom by sulphur when the based quinoxaline ring was substituted, in the seventh position, with chlorine group and methyl group reported elsewhere [13]. This investigation was conducted by weight loss, polarisation and impedance methods. The thermodynamic parameters of adsorption onto mild steel were determined and the nature of inhibitors adsorption process was also studied and discussed.

2. EXPERIMENTAL PROCEDURE

2.1. Material preparation

Mild steel strips containing (in wt%) 0.09 P, 0.38 Si, 0.01 Al, 0.05 Mn, 0.21 C, 0.05 S and balance iron were used for electrochemical and gravimetric studies. Mild steel specimens were mechanically polished on wet SiC papers (400, 600, 1000 and 1200), washed with double-distilled water, and dried at room temperature before being immersed in the acid solution. The aggressive solution (1 M HCl), used as blank, was made from Riedel-de Haën and prepared by dilution of analytical grade 37%. The molecular structures of the studied quinoxaline, names and the corresponding abbreviations are shown in Table 1. Appropriate concentrations of inhibitors were prepared with double-distilled water addition. The concentration range of inhibitors employed was 10^{-6} – 10^{-3} M in 1 M HCl. The temperature was controlled at 308 K without bubbling in a double walled glass cell.

Table 1. Molecular structures, names and abbreviations of the studied quinoxaline derivatives

Quinoxalinee Formula	Name	Abbreviation
	3-methylquinoxalin-2(1H)-one	Q=O
	3-methylquinoxalin-2(1H)-thione	Q=S
	7-chloro-3-methylquinoxalin-2(1H)-one	Cl-Q=O
	7-chloro-3-methylquinoxalin-2(1H)-thione	Cl-Q=S

2.2. Weight loss measurements, WL

Gravimetric experiments were investigated in a double-walled glass cell equipped with a thermostat cooling condenser. The solution volume was 100 cm^3 and the temperature of 308 K was controlled thermostatically. The mild steel specimens were rectangular in the form (1cm × 4cm × 0.06cm). The weight loss of mild steel in 1 mol L^{-1} HCl with and without addition of inhibitors was determined after an immersion period in acid for 6 h. After the corrosion test, the specimens were carefully washed in double distilled water, dried and then weighted. Duplicate experiments were performed in each case, and the mean value of the weight loss is reported. Weight loss allowed us to calculate the mean corrosion rate as expressed in mg cm^{-2} h^{-1}.

2.3. Current – Voltage measurements, I-E

Electrochemical measurements were carried out in a conventional three-electrode glass cell with a platinum counter electrode and a saturated calomel electrode (*SCE)* as reference. All tests were performed in continuously stirred conditions at room temperature; all tests were performed at 308 K. Potentiodynamic curves-polarization experiments were undertaken by (Radiometer-analytical PGZ 100) and controlled with analysis software (Voltamaster 4). The mild steel electrode was maintained at open circuit conditions (corrosion potential, E_{corr}) for 1 h and thereafter pre-polarized at -800 mV for 10 min. After this scan, the potential was swept to anodic potentials. The cathodic branch was always determined first; the open-circuit potential was then re-established and the anodic branch determined. The anodic and cathodic polarization curves were recorded by a constant sweep rate of 1 mV s^{-1}.

2.4. Electrochemical impedance spectroscopy measurements, EIS

The electrochemical impedance spectroscopy (*EIS*) measurements were performed using a transfer function analyser (Voltalab PGZ 100), with a small amplitude a.c. signal (10 mV rms) over a frequency domain from 100 kHz to 10 mHz at 308 K with 5 points per decade. Computer programs automatically controlled the measurements performed at rest potentials after 1 h of immersion at E_{corr}. The impedance diagrams were given in the Nyquist representation.

3. RESULTS AND DISCUSSION

3.1. Gravimetric tests, WL

Gravimetric measurements of mild steel were investigated in 1 M HCl in the presence and absence of various concentrations of the studied quinoxaline molecules. The mass loss is determined after removing the corrosion products from the metal solution in accordance to the ASTM G1-67. The degree of dissolution depends on the surface area of the metal specimen and time of exposure; hence, the amount of corrosion is given with respect to these two parameters. The resulting quantity, corrosion rate, W_{corr}, is thereby the fundamental measurement in corrosion. W_{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):

$$W_{corr} = \frac{m_i - m_f}{S\,t} \tag{1}$$

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

The effect of all addition quinoxaline molecules is studied at different concentrations, on mild steel corrosion, in 1 M HCl medium, during 6 h of immersion period at 308 K. The values of the corrosion rate, W_{corr}, and inhibiting efficiency, $E_{WL}\%$, are given in Table 2. $E_{WL}\%$ was estimated by the following relation (2):

$$E_{WL}\% = \frac{W_{corr} - W_{corr/inh}}{W_{corr}} \times 100 \tag{2}$$

W_{corr} and $W_{corr/inh}$ are the corrosion rate of steel without and with each inhibitor, respectively.

Maximum $E_{WL}\%$ for each substance was achieved at 10^{-3} mol L^{-1} and any further increase in concentration did not cause any appreciable change in the performance of the studied inhibitors. The variation of the inhibitory effect mainly depends on the type and the presence of chlorine group as well as the substitution of oxygen atom by sulphur one. It is clear that the mild steel corrosion rate values decreases with the concentration of the undertaken inhibitors, and in turn the inhibiting efficiency increases to reach circa 90% at 10^{-3} mol L^{-1} of Q=S.

The results drawn on Table 2 clearly exemplify a decrease in the corrosion rate in the presence of all products. This effect is hugely marked at higher concentration of quinoxaline inhibitors. For the inhibitor, Cl-Q=O especially studied at 10^{-3} mol L^{-1} gave only 56.5 as $E_{WL}\%$ at the limit of its solubility. The authors have suggested uninteresting to expand more studies neither at lower concentrations nor with other techniques.

These results clearly show the beneficial effect of the substitution of an oxygen atom by a sulphur one. The order of inhibiting efficiency of the investigated compounds, with respect to this last substitution decrease in the following order:

Q=S > Q=O and Cl-Q=S > Cl-Q=O.

Table 2. Gravimetric results of the mild steel corrosion with and without addition of quinoxaline inhibitors studied at 308 K after 6 h of immersion in 1 M HCl

Inhibitor	Concentration C / mol L^{-1}	Corrosion weight loss W_{corr} / mg cm^{-2} h^{-1}	E_{WL} %
Blank	00	1.15	–
Q=O	10^{-6}	0.89	22.6
	10^{-5}	0.67	41.7
	5×10^{-5}	0.52	54.8
	10^{-4}	0.46	60.0
	5×10^{-4}	0.32	69.5
	10^{-3}	0.28	75.6
Q=S	10^{-6}	0.65	43.5
	10^{-5}	0.48	58.3
	5×10^{-5}	0.43	62.6
	10^{-4}	0.33	71.3
	5×10^{-4}	0.23	80.0
	10^{-3}	0.12	89.6
Cl-Q=O	10^{-3}	0.5	56.5
Cl-Q=S	10^{-6}	0.82	28.7
	10^{-5}	0.62	46.0
	5×10^{-5}	0.50	56.5
	10^{-4}	0.42	63.5
	5×10^{-4}	0.31	73.0
	10^{-3}	0.25	78.3

The high inhibitive performance of Q=S suggests a strong bonding of this quinoxaline molecule onto the metal surface due to the presence of several lone pairs from heteroatom (nitrogen and sulphur) and π-orbitals, blocking the active sites and therefore decreasing the corrosion rate. Moreover, the high $IE_{WL}\%$ of Q=S can be imputed to the presence of thioxo group on the pyrazine ring, which gives the possibility of πd- πd bond formation resulting from overlap of 3d electrons from Fe atom and the 3d vacant orbital of sulphur atom [14]. Indeed, Chetouani et al. [15,16] have reported the importance of sulphur atom in the drastic change of adsorption mechanism. Furthermore, Brandt et al. [17] reported that the sulphur atom represents the active centre of aliphatic sulphides in their interaction with the metal surface.

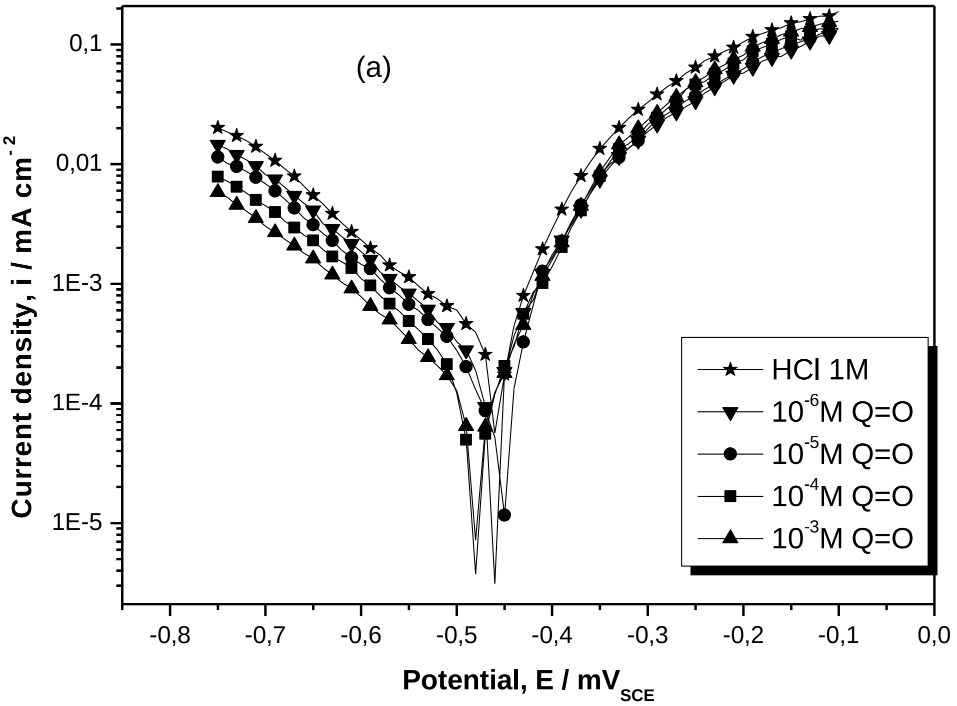
The protective properties of such compounds are probably due to the interaction of π electrons of pyrazine and phenyl rings as well as the presence of electron donor groups (S, N and O) through which the ability is easy to form bonds with transition metals such as mild steel. The sulphur atom provides a high electron density compared to the oxygen atom and it was found that $IE_{WL}\%$ increases with electron density [18].

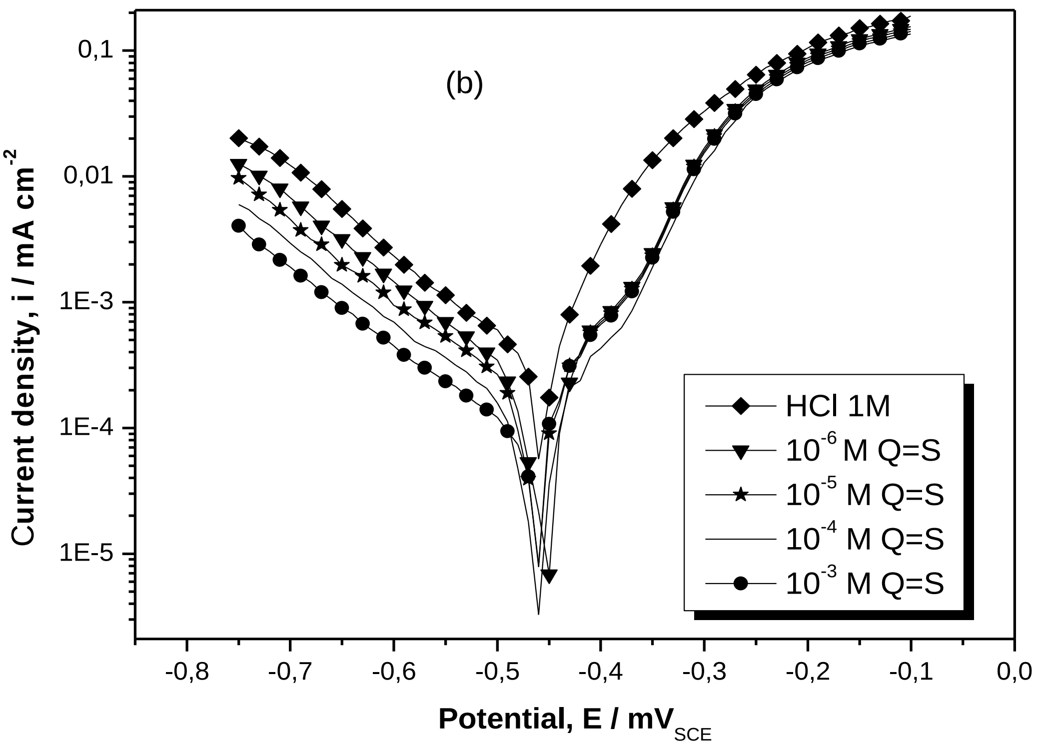
Careful inspection of these results showed that, at the same inhibitor concentration, the order of decreasing inhibition efficiency of the undertaken quinoxaline is as follows:

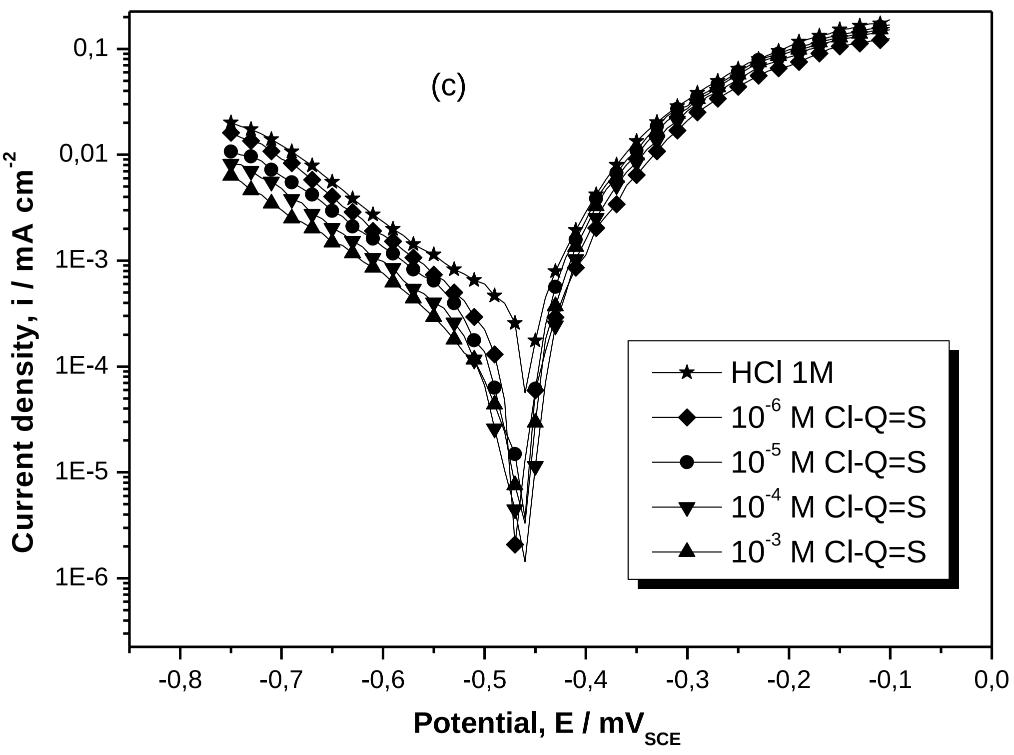
Q=S > Cl-Q=S > Q=O > Cl-Q=O.

3.2. Polarisation measurements, I – E

Polarization measurements have been carried out in order to gain knowledge concerning the kinetics of the anodic and cathodic reactions. Figure 1 shows the potentiodynamic curves obtained in the presence and absence of the studied inhibitors at different concentrations and temperature of 308 K in 1 M HCl, after pre-polarizing the electrode at its E_{corr} for an hour in order to obtain steady-state measures. As it can be seen, only cathodic reaction is affected by the presence of Q=O and Cl-Q=S whereas both cathodic and anodic reactions of mild steel electrode corrosion were inhibited with the concentration increase of Q=S. This behaviour is, for the last product, more pronounced in the cathodic branch whereas in the anodic branch, the decrease observed at 10^{-5} M of Q=S remains the same even at higher concentrations 10^{-3} M. Q=S then appears to slow down the cathodic reaction to greater extents than anodic one. No definite trend was defined in the shift of corrosion potential, E_{corr} values in the large domain of the studied Q=S concentrations. The same behaviour has been registered with Q=O and Cl-Q=S. These results suggest that the addition of quinoxaline derivatives under study reduce anodic dissolution of mild steel for Q=S and also retard the hydrogen evolution reaction for Q=S, Cl-Q=S and Q=O.




(b)
Current density, i / mA cm^{-2}
0,1
0,01
1E-3
1E-4
1E-5
-0,8
-0,7
-0,6
-0,5
-0,4
-0,3
-0,2
-0,1
0,0
Potential, E / mV$_{SCE}$
HCl 1M
10^{-6} M Q=S
10^{-5} M Q=S
10^{-4} M Q=S
10^{-3} M Q=S


(c)
Current density, i / mA cm^{-2}
0,1
0,01
1E-3
1E-4
1E-5
1E-6
-0,8
-0,7
-0,6
-0,5
-0,4
-0,3
-0,2
-0,1
0,0
Potential, E / mV$_{SCE}$
HCl 1M
10^{-6} M Cl-Q=S
10^{-5} M Cl-Q=S
10^{-4} M Cl-Q=S
10^{-3} M Cl-Q=S

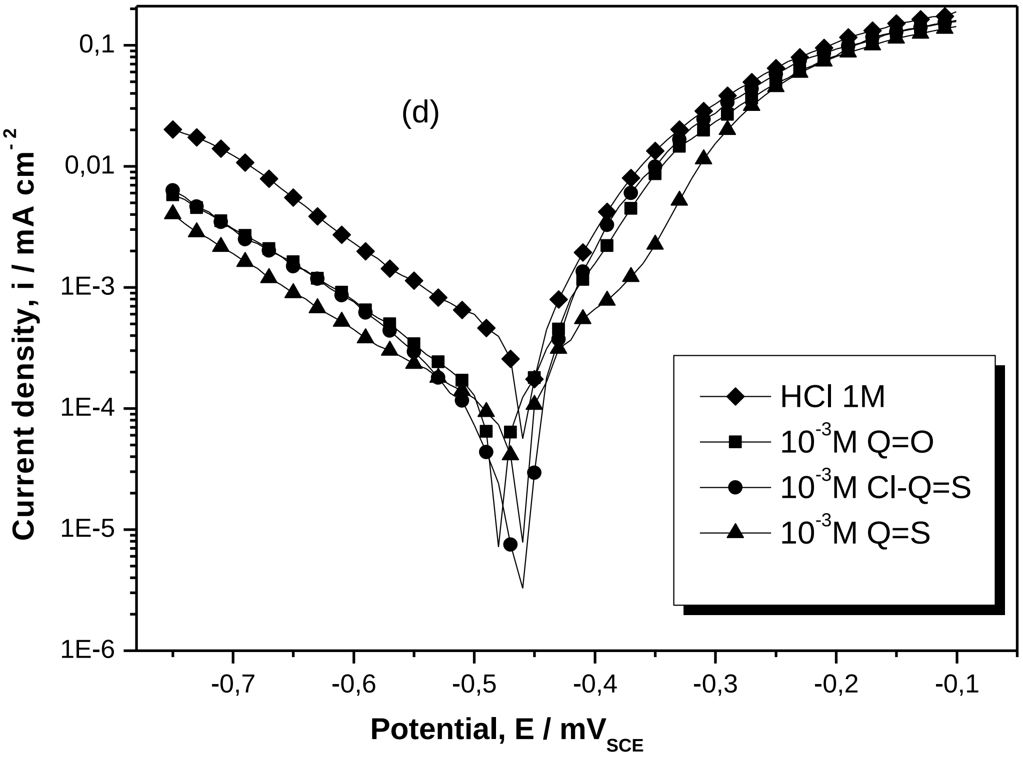


Figure 1. Potentiodynamic polarization curves obtained for mild steel at 308 K in 1 M HCl at various concentrations of the studied inhibitors (a) Q=O, (b) Q=S, (c) Cl-Q=S and (d) at 10^{-3} M of all the examined compounds

Cathodic current potential curves give rise to parallel Tafel lines indicating that the hydrogen discharge is activation-controlled and the addition of quinoxaline derivatives does not affect the mechanism process of hydrogen reduction. This stipulates that the inhibition of hydrogen evolution occurs by simple adsorption mode and the mechanism remain the same in inhibited and uninhibited media. In anodic domain, the addition of Q=S leads to a decrease in the current densities in large potential domain. It is also observed that for potentials higher than -350 mVsce, the Q=S starts to be desorbed. In this case desorption of Q=S is raised more than its adsorption.

Table 3 exemplifies electrochemical corrosion kinetic parameters, such as corrosion potential E_{corr}, corrosion current density i_{corr}, cathodic Tafel slope β_c and inhibiting efficiency $E_{I-E}\%$ given as follows in equation (3).

$$E_{I-E}\% = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100 \qquad (3)$$

i^0_{corr} and i_{corr} are the corrosion current densities values without and with inhibitors, respectively.

Table 3. Values of electrochemical parameters evaluated from the cathodic current-voltage characteristics for the system electrode/1 M HCl with and without added inhibitors at 308 K

Inhibitor	Concentration mol L^{-1}	E_{corr} mV_{sce}	$\lvert \beta_c \rvert$ mV dec^{-1}	i_{corr} $\mu A\ cm^{-2}$	E_{I-E} %
Blank	00	-460	160	350	-
Q=O	10^{-6}	-460	158	240	31.4
	10^{-5}	-450	155	161	54.0
	10^{-4}	-475	150	139	60.3
	10^{-3}	-460	156	105	70.0
Q=S	10^{-6}	-450	162	200	42.8
	10^{-5}	-460	165	150	57.1
	10^{-4}	-455	163	106	69.7
	10^{-3}	-470	165	52	85.1
Cl-Q=S	10^{-6}	-470	140	250	28.6
	10^{-5}	-460	150	160	54.3
	10^{-4}	-470	145	120	65.7
	10^{-3}	-460	150	80	77.1

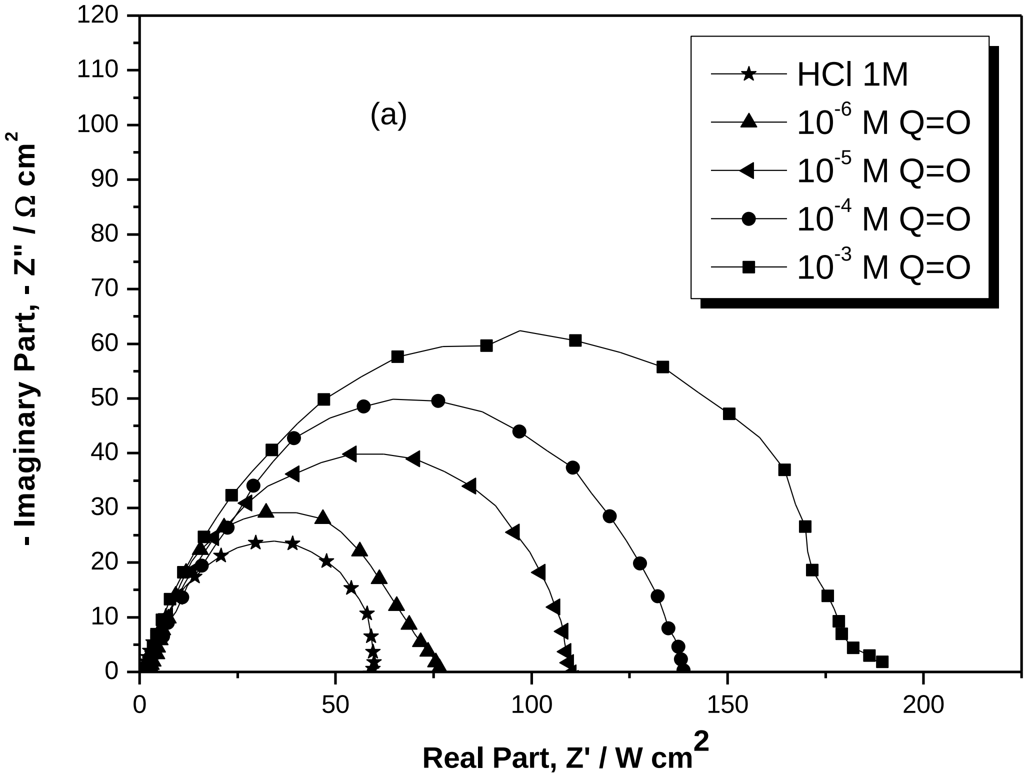
These values were extracted from the extrapolation of the cathodic slope to the free corrosion potential for quinoxaline derivatives at the considered concentrations. The experimental data shows that all the studied quinoxaline decreased i_{corr} values at all concentrations, and a maximum decrease in i_{corr} value was obtained at 10^{-3} M. E_{I-E}% increases with inhibitor concentration reaching a maximum value at 10^{-3} M. The values of maximum inhibiting efficiency are lower than that obtained by gravimetric test as they are recorded at a much shorter time interval and reflect the corrosion behaviour at the initial stage.

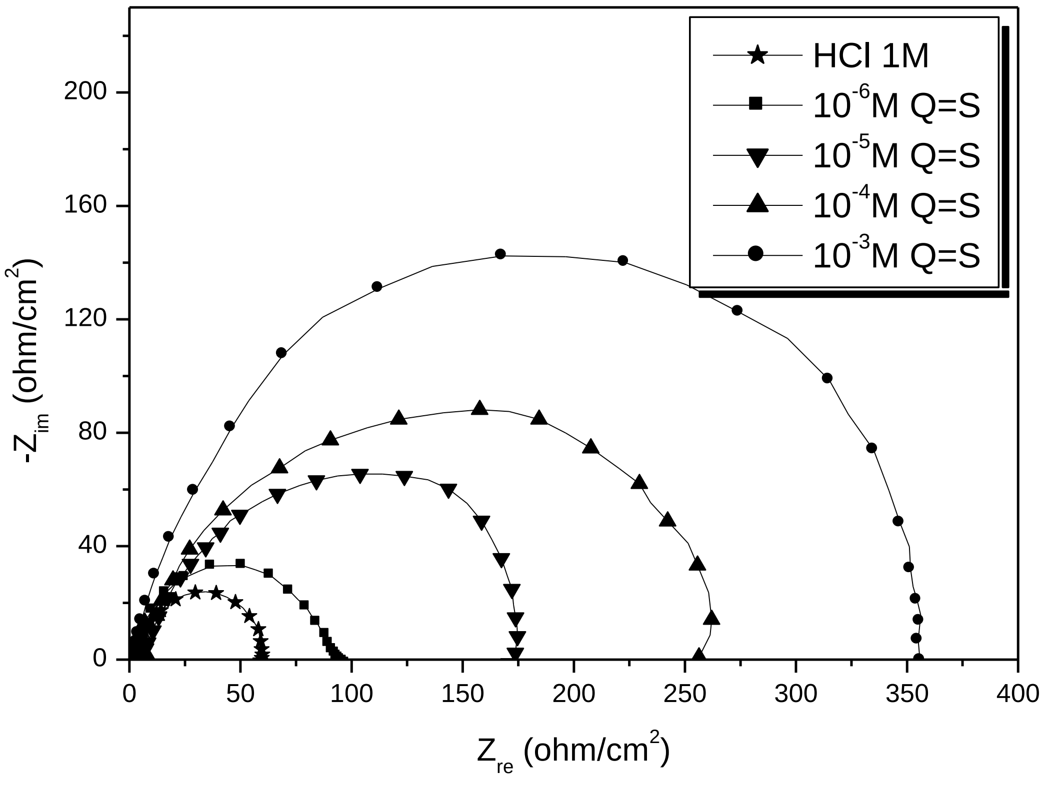
The conclusions drawn from the polarization curves confirm those obtained from gravimetric test in terms of the order of decreasing inhibition efficiency of the undertaken quinoxaline as follows:

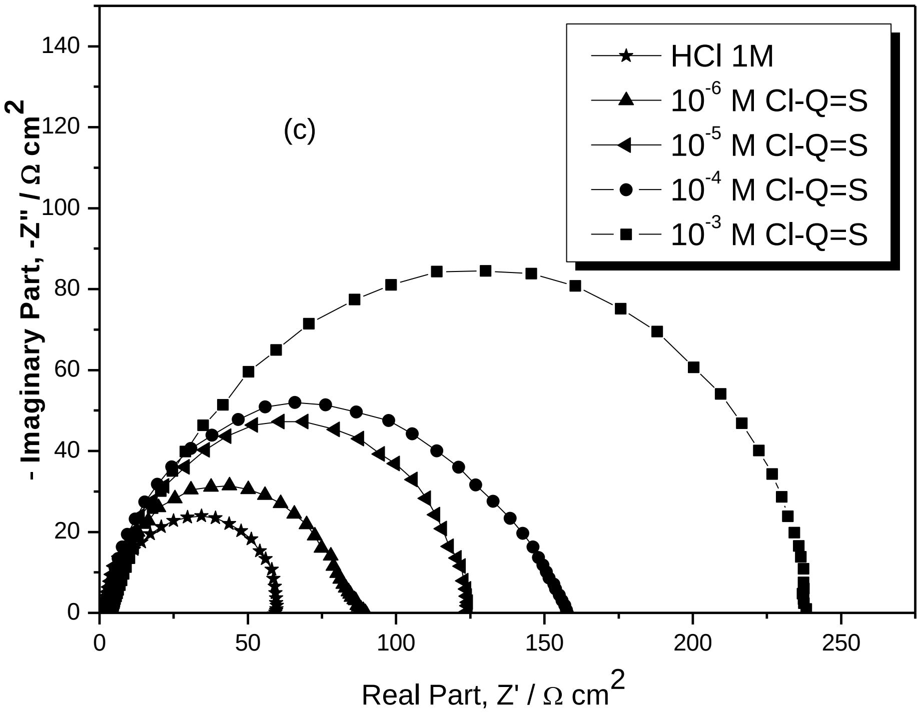
Q=S > Cl-Q=S > Q=O.

3.3. Electrochemical impedance measurements, EIS

The EIS technique has been extensively used with other electrochemical methods to interpret the corrosion and corrosion inhibition of metals and alloys including mild steel in severe environments such as neutral and acidic media [19-24]. The corrosion behaviour of mild steel in 1 M HCl solution in the presence of the studied inhibitors was carried out by EIS at 308 K after an hour of hold time immersion at open circuit potential in the range of 100 kHz to 10 mHz. Representative Nyquist diagrams in inhibited and uninhibited solutions containing different concentrations of Q=O, Q=S and Cl-Q=S are shown in Figure 2.


(a)
HCl 1M
10^-6 M Q=O
10^-5 M Q=O
10^-4 M Q=O
10^-3 M Q=O
- Imaginary Part, - Z'' / Ω cm²
Real Part, Z' / W cm²
0
10
20
30
40
50
60
70
80
90
100
110
120
0
50
100
150
200


HCl 1M
10^-6M Q=S
10^-5M Q=S
10^-4M Q=S
10^-3M Q=S
-Z_im (ohm/cm²)
Z_re (ohm/cm²)
0
40
80
120
160
200
0
50
100
150
200
250
300
350
400



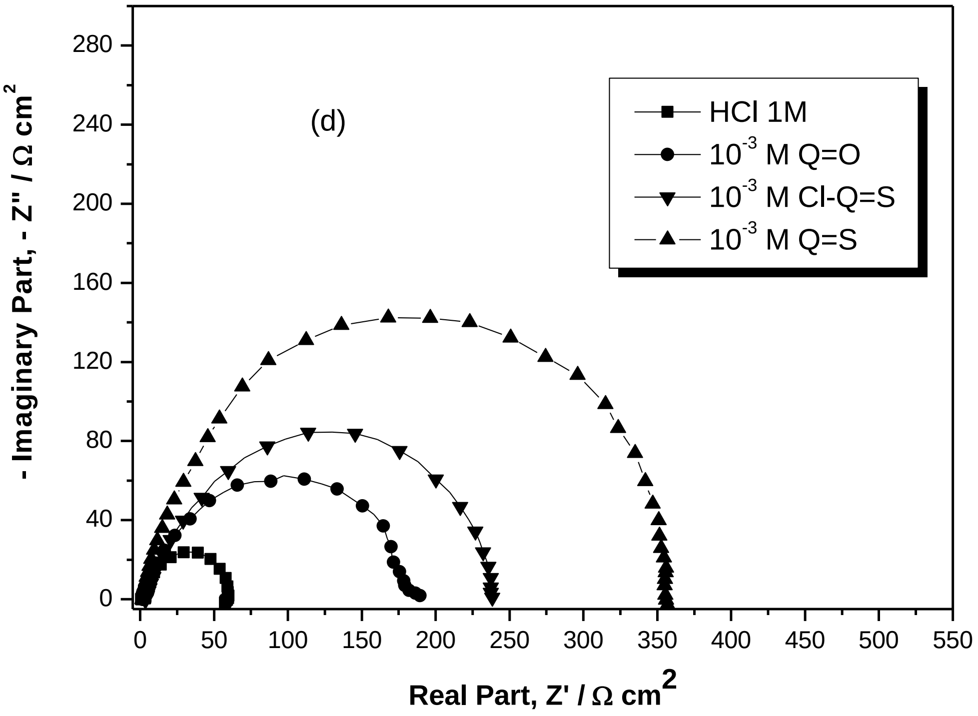


Figure 2. Nyquist diagrams obtained for mild steel at 308 K in 1 M HCl at various concentrations of the studied inhibitors (a) Q=O, (b) Q=S, (c) Cl-Q=S (d) at 10^{-3} M of all the examined compounds

The results of impedance responses obtained are consistent with literature [25]. The impedance diagrams obtained are not perfect semicircles and this difference has been attributed to frequency dispersion [26-28] imputed to different physical phenomena such as roughness and non homogeneities of the solid surface.

The EIS results were interpreted in terms of an equivalent circuit as described elsewhere [25]. It is to be noted from the whole diagrams that the impedance response of mild steel in free HCl solution has significantly changed after the addition of quinoxaline derivatives in the corrosive medium. This reflects that the impedance of inhibited substrate increases with rising inhibitors concentration and accordingly the inhibiting efficiency.

Table 4 summarises the characteristic kinetic parameters associated to this impedance study such as the charge-transfer resistance R_{ct}, the double layer capacitance C_{dl} and the inhibiting efficiency E_{imp} %.

Table 4. EIS data of mild steel in 1 M HCl containing different concentrations of the studied inhibitors at 308 K

Inhibitor	**Concentration mol L^{-1}**	**R_{ct} Ω cm^2**	**C_{dl} µF cm^{-2}**	**E_{imp} %**
Blank	00	60	490	–
Q=O	10^{-6}	75	150	20
	10^{-5}	110	120	45.6
	10^{-4}	140	105	57.2
	10^{-3}	180	60	66.6
Q=S	10^{-6}	90	108	33.3
	10^{-5}	175	92	65.7
	10^{-4}	260	73	76.9
	10^{-3}	350	67	82.8
Cl-Q=S	10^{-6}	88	78	31.8
	10^{-5}	125	64	52.0
	10^{-4}	160	53	62.5
	10^{-3}	240	49	75.0

The inspection of values given in Table 4 shows that the R_{ct} increased with the concentration of the quinoxaline derivatives and reached a maximum value of 350 Ω cm^2 at 10^{-3} M of Q=S. The change of R_{ct} can be related to the gradual replacement of water molecules by the inhibitors over the metal surface and in view of that leads to decrease in the number of active sites responsible of corrosion reaction. As a result, the increase of R_{ct} values can be attributed to the formation of protective film at the mild steel/1M HCl interface. In addition, the values of double layer capacitance, C_{dl}, decreased with increasing the studied inhibitors concentration. The decrease of C_{dl} is generally interpreted in the literature as a result of a decrease of the local dielectric constant of the inhibitor film and/or an increase of the thickness of the adsorbed protective film enhancing then the corrosion resistance of the mild steel.

The inhibiting efficiency derived from ac impedance investigations is calculated from R_{ct} and is as follows, eq. (4):

$$E_{imp}\% = \frac{R_{ct} - R_{ct}^{0}}{R_{ct}} \times 100 \qquad (4)$$

R_{ct} and R'_{ct} are the polarisation resistances with and without the studied inhibitors, respectively.

The ac impedance investigations in 1 M HCl show that all quinoxaline derivatives exhibit inhibitor properties, the best being Q=S. It is found that the inhibiting efficiency, $E_{imp}\%$ increases with the compound concentration (Table 4) and it depends on the substitution of an oxygen atom by a sulphur one as well as the presence of chlorine group on the phenyl moiety. Based on the inhibitive properties of the examined quinoxaline, these last can be ranked as follows: Q=S > Cl-Q=S > Q=O.

3.4. Adsorption isotherm and thermodynamic parameters

The adsorption isotherm can be determined if the inhibitor effect is due mainly to the adsorption on metallic surface (i.e. to its blocking). The adsorption isotherm type can provide additional information about the tested compounds properties. The fractional coverage surface (θ) can be easily determined from ac impedance, potentiodynamic curves or weigh loss by the ratio *E%/100*. In the present study, the inhibiting efficiency is evaluated from weigh loss measurements. If one assumes that the values of $E_{WL}\%$ do no differ substantially from θ as shown in Table 2. Several adsorption isotherms were assessed. The best fitted straight line (Fig. 3) is obtained from the plot of C_{inh}/θ versus C_{inh} with nearly unit slope and the best fits are obtained with Langmuir's adsorption isotherm as given in the equation 5:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (5)$$

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

From the intercepts of the straight lines C_{inh}/θ-axis, K_{ads} values can be derived. The calculated equilibrium constant of Q=S, Q=O and Cl-Q=S are 50203.32, 43902.01 and 51238.4 L mol^{-1}, respectively. The constant of adsorption is related to the standard free energy of adsorption, ΔG°_{ads}, by the following equation (6):

$$K_{ads} = \frac{1}{55,55}\exp(-\frac{\Delta G^{\circ}_{ads}}{RT}) \qquad (6)$$

55.55 represents the concentration of water in solution in mol L^{-1}, R is the universal gas constant and T is the absolute temperature. The standard free energy of adsorption, $\Delta_{ads}G^0$ can be calculated. The negative values of $\Delta_{ads}G^0$ ensure the spontaneity of the adsorption process and stability of the adsorbed layer on mild steel surface. It is well known that the absolute values of $\Delta_{ads}G^0$ of order of 20 kJ mol^{-1} or lower indicate a physisorption; while those of order of 40 kJ mol^{-1} or higher are associated with chemisorption [29]. Values of $\Delta_{ads}G^0$ for Q=S, Q=O and Cl-Q=S are -38.003, -37.66 and -38.056 kJ mol^{-1}, respectively. It is suggested that the adsorption mechanism of the investigated inhibitors on the mild steel surface in 1 M HCl solution involves two types of interaction; chemisorption and physisorption [30].

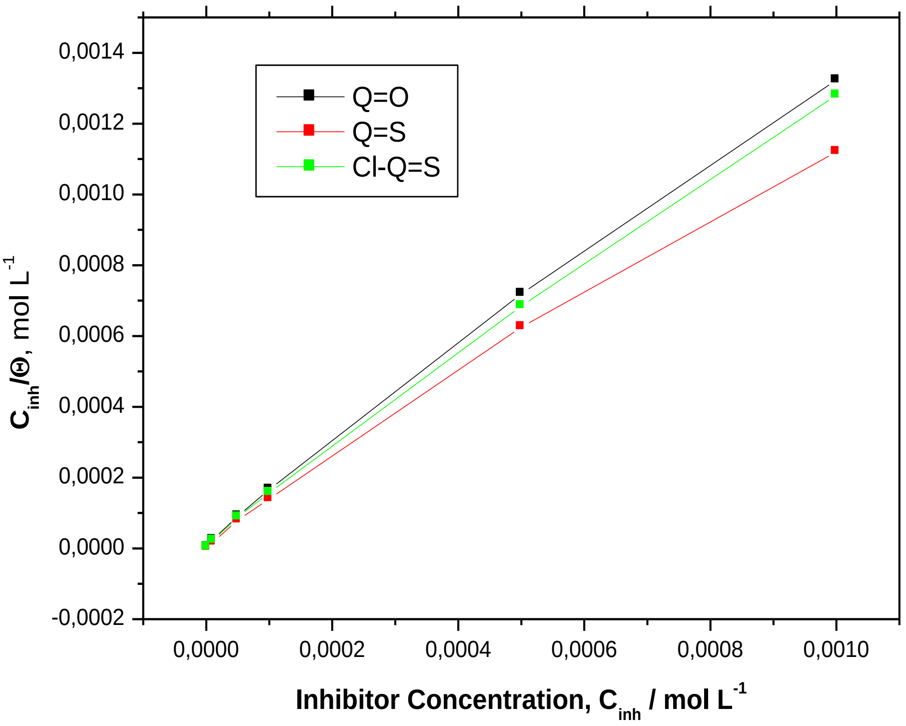


Figure 3. Langmuir adsorption isotherm plot for mild steel in 1 M HCl at different concentrations of the studied inhibitors

Hence it can be suggested that each inhibitors adsorb on metallic surface forming strong chemisorption bonds. This is in fact possible in view of the presence of unshared electron pairs in the organic compounds molecules and taking into consideration the behaviour of Fe as electrons acceptor as its d-submonolayer is incomplete. The inhibitors studied may then be adsorbed via donor–acceptor interactions between the π-electrons of the aromatic systems and the unshared electrons pairs of the heteroatoms (-N, -O) to form a bond with the vacant d orbital of the iron atom on the metal surface, which act as a Lewis acid, leading to the formation of a protective chemisorbed film.

Beside the fact that the inhibition phenomenon can be imputed to the presence of empty d-orbital in the Fe which led to an easier coordinate bond formation between the metal and inhibitors, these last contain nitrogen and oxygen atoms which are easily protonated in HCl medium. Therefore, physical adsorption is also possible via electrostatic interaction between a negatively charged surface, which is provided with a specifically adsorbed chloride anion on mild steel, and the positive charge of the inhibitors [31].

3.5. Effect of chemical structure of the studied quinoxaline on corrosion inhibition

Corrosion inhibition of mild steel in 1 M HCl by the quinoxaline derivatives as examined by means of chemical (WL) and electrochemical (I-E, EIS) techniques were found to depend on both the concentration and the nature of the inhibitor. Moreover, after a recent study on quinoxaline substituted in the seventh position with a methyl group instead of chlorine group, the results of inhibiting efficiency are as follows: Me-Q=S and Me-Q=O, 93,27 and 81, respectively [13]. Afterwards the order of decreasing inhibition efficiency of the whole quinoxaline derivatives Me-Q=O > Q=O > Cl-Q=O and Me-Q=S > Q=S > Cl-Q=S. Increasingly, for the same graft element, methyl or chloride, the substitution of the oxygen atom by the sulfur is as follows:

Me-Q=S > Me-Q=O, Q=S > Q=O > and Cl-Q=S > Cl-Q=O.

It is obvious from the above sequence that, quinoxaline molecules containing electron donating group (Me-Q=S and Me-Q=O) are more efficient than those containing electron withdrawing group (Cl-Q=S and Cl-Q=O). Indeed, the electron donating group (methyl group) enhances adsorption and increases the surface area covered by the inhibitor because the atoms adjacent to the π system activate the aromatic ring then increasing the electron density on the ring through a resonance donating effect. Strongly activating electron donating groups add electron density to the π system making it more nucleophilic and accordingly increase the inhibiting efficiency. In contrast, the electron withdrawing groups, with π bonds to electronegative atoms adjacent to the π system deactivate the aromatic ring by decreasing the electron density on the ring through a resonance withdrawing effect. Hence, the electron withdrawing group (chlorine group) removes electron density from the π system making it less nucleophilic and thereby with lower inhibition efficiency. Similar results have been obtained in the study of mild steel corrosion inhibition of some phenolic compounds in hydrochloric acid [32].

4. CONCLUSION

The following results can be drawn from this study:

1. Reasonably good agreement was observed between the data obtained from gravimetric, potentiodynamic polarization and electrochemical impedance spectroscopy techniques.
2. Q=O and Cl-Q=S slow down the cathodic reaction then considered as cathodic type inhibitors whereas Q=S slows down the cathodic reaction to greater extents than the anodic one which suggests that Q=S mainly acts as mixed-type inhibitor.
3. The adsorption of the studied quinoxaline derivatives is well described by the Langmuir adsorption isotherm. All values of the standard Gibbs energy of adsorption are negative and less in absolute values $|\Delta_{ads}G°|$ than 40 kJ mol^{-1}. These results confirm that both of chemisorption and physisorption control the adsorption phenomenon.

References

1. Nnabuk O. Eddy, Benedict I. Ita, Nkechi E. Ibisi, Eno E. Ebenso, *Int. J. Electrochem. Sci*., 6 (2011) 1027.
2. L. Maria Rodriguez-Valdez, A. Martinez-Villafane, D. Glossman-Mitnik, *J. Molec. Struc : THEOCHEM*, 713 (2005) 65.
3. S. Aloui, I. Forsal, M. Sfaira, M. Ebn Touhami, M. Taleb, M.F. Baba, M. Daoudi, *Portugaliae, Electrochim. Acta*, 27 (2009) 599.
4. B. Zerga, R. Saddik, B. Hammouti, M. Taleb, M. Sfaira, M. Ebn Touhami, S.S. Al-Deyab, N. Benchat, *Int. J. Electrochem. Sci*., 7 (2012) 631.
5. B. Zerga, B. Hammouti, M. Ebn Touhami, R. Touir, M. Taleb, M. Sfaira, M. Bennajeh, I.Forsal. *Int. J. Electrochem. Sci*., 7 (2012) 471.
6. Z. El Adnani, M. Mcharfi, M. Sfaira, A.T. Benjelloun, M. benzakour, M. Ebn Touhami, B. Hammouti, M. Taleb, *Int. J. Electrochem. Sci*., 7 (2012) 3982.
7. B. Zerga, A. Attayibat, M. Sfaira, M. Taleb, B. Hammouti, M. Ebn Touhami, S. Radi, Z.Rais, *J. Appl. Electrochem*., 40 (2010) 1575.
8. Y. Aouine, M. Sfaira, M. Ebn Touhami, A. Alami, B. Hammouti, M. Elbakri, A. El Hallaoui, R. Touir, *Int. J. Electrochem. Sci*., 7 (2012) in press.
9. M.B. Cisse, B. Zerga, F. El Kalai, M. Ebn Touhami, M. Sfaira, M. Taleb, B. Hammouti, N. Benchat, S. El kadiri, A.T. Benjelloun, *Surf. Rev. Lett*., 18 (2011) 303.
10. Y. Abboud, A. Abourriche, T. Saffaj, M. Berrada, M. Charrouf, A. Bennamara, N. Al Himidi, H. Hannache, *Mater. Chem. Phys*. 105 (2007) 1.
11. A.Zarrouk, B. Hammouti, A. Dafali, M. Bouachrine , H. Zarrok, S. Boukhris, S.S. Al-Deyab, doi:10.1016/j.jscs.2011.09.011.
12. I.B. Obot, N.O. Obi-Egbedi, N.W. Odozi, *Corros. Sci*. 52 (2010) 923.
13. K. Adardour, O. Kassou, R. Touir, M. Ebn Touhami, H. ElKafsaoui, H. Benzeid, El M.Essassi, M. Sfaira, *J. Mater. Environ. Sci*. 1 (2010) 129.
14. B. Bonnelly, T.C. Downie, R. Grzekowiak, H.R. Hamburg, D. Short, *Corros. Sci*. (1978)18.
15. A.Chetouani, B. Hammouti, A. Aouniti, N. Benchat, T. Benhadda, *Prog. Org. Coat*. 45 (2002) 375.
16. B.Chetouani, A. Aouniti, B. Hammouti, N. Benchat, T. Benhadda, S. kertit, *Corros. Sci*. 45 (2003) 1679.
17. H. Brandt, M. Fischer, K. Schawabe, *Corros. Sci*. 10 (1970) 631.

18. M. Bouklah, N. Benchat, A. Aouniti, B. Hammouti, M. Benkaddour, M. Lagrenée, H.Vezin, F. Bentiss, *Prog. Org. Coat*., 51 (2004) 118.
19. R. Touir, N. Dkhireche, M. Ebn Touhami, M. El Bakri, A. Rochdi, R. A. Belakhmima, J.Saudi Chem. Soc., (2011) DOI: 10.1016/j.jscs.2011.10.020.
20. R Touir, M. Cenoui, M. EI Bakri, M. Ebn Touhami, *Corros. Sci.*, 50 (2008) 1530.
21. R. Touir, N. Dkhirech, M. Ebn Touhami, M. Lakhrissi, B. Lakhrissi, M. Sfaira, *Desalination*, 249 (2009) 922.
22. M. Cenoui, N. Dkhirech, O. Kassou, M. Ebn Touhami, R. Touir, A. Dermaj, N. Hajjaji, *J. Mater. Environ. Sci*., 1 (2010) 84.
23. R. Touir, N. Dkhireche, M. Ebn Touhami, M. Sfaira, O. Senhaji, J.J. Robin, B. Boutevin, M. Cherkaoui, *Mater. Chem. Phys*., 122 (2010) 1.
24. N. Dkhireche, M. Ebn Touhami, H. Oudda, R. Touir, M. Sfaira, B. Hammouti, O.Senhaji, R. Taouil, *Int. J. Electrochem. Sci*., 7 (2012) in press.
25. F. Bentiss, M. Outrite, M. Traisnel, H. Vezin, M. Lagrenée, B. Hammouti, S.S. Al-Deyab,C. Jama, *Int. J. Electrochem. Sci*., 7 (2012) 1699.
26. M. Sfaira, A. Srhiri, M. Keddam, H. Takenouti, *Electrochim. Acta*, 44 (1999) 4395.
27. M. Sfaira, A. Srhiri, H. Takenouti, M.M. de Ficqulmont-Loizos, A. Ben Bachir, M. Khalakhil, *J. Appl. Electrochem*., 31 (2001) 537.
28. S. Duval, M. Keddam, M. Sfaira, A. Srhiri, H. Takenouti, *J. Electrochem. Soc*. 149 (2002) B520.
29. E. Khamis, F. Bellucci, R.M. Latanision, E.S.H. El-Ashry, *Corrosion* 47 (1991) 677.
30. W. Li, Q. He, C. Pei, B. Hou, *Electrochim. Acta* 52 (2007) 6386.
31. H. Ashassi-Sorkhabi, B. Shaabani, D. Seifzadeh, *Appl. Surf. Sci*. 239 (2005) 154.
32. M. Abdallah, B.H. Asghar, I. Zaafarany, A.S. Fouda, *Int. J. Electrochem. Sci.* 7 (2012) 282.