

Contents lists available at ScienceDirect

Journal of Molecular Liquids



Experimental and theoretical studies for mild steel corrosion inhibition in 1.0 M HCl by three new quinoxalinone derivatives



A. Tazouti^a, M. Galai^a, R. Touir^{a,b}, M. Ebn Touhami^a, A. Zarrouk^{c,*}, Y. Ramli^d, M. Saraçoğlu^e, S. Kaya^f, F. Kandemirli^g, C. Kaya^f

^a Laboratory of Materials, Electrochemistry and Environment, Faculty of Science, Ibn Tofail University, PB 133-14050, Kénitra, Morocco

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

^c LCAE-URAC18, Faculty of Science, Mohammed first University, Po Box 717, 60000 Oujda, Morocco

^d Laboratoire de Chimie Thérapeutique, Faculté de Médecine et de Pharmacie de Rabat, Université Mohamed V, Av. Med. Belarbi Elalaoui, BP 6203, Rabat-Instituts, Rabat, Morocco

^e Faculty of Education, Erciyes University, 38039 Kayseri, Turkey

^f Department of Chemistry, Faculty of Science, Cumhurivet University, 58140, Sivas, Turkey

^g Department of Biomedical Engineering, Faculty of Engineering and Architecture, Kastamonu University, 37150, Kastamonu, Turkey

ARTICLE INFO

Article history: Received 23 November 2015 Received in revised form 21 February 2016 Accepted 2 March 2016 Available online xxxx

Keywords: Ouinoxalinone derivatives Mild steel Corrosion inhibition 1.0 M HCl Electrochemical techniques Computational chemistry

ABSTRACT

(E)-3-styrylquinoxalin-2(1H)-one Three quinoxalinone derivatives, namely (SQ), (E)-3-(4methoxystyryl)quinoxalin-2(1H)-one (MOSQ) and (E)-3-(4-methoxystyryl)-7-methylquinoxalin-2(1H)-one (MOSMQ) were synthesized and characterized. Thus, their inhibition effects on mild steel corrosion in 1.0 M HCl medium were investigated using weight loss method, electrochemical measurements. The effect of temperature on the corrosion behavior of mild steel was studied in the range of 298-328 K. Polarization measurements indicated that, the studied compounds act as a mixed type inhibitors, the inhibition efficiency depends on their concentrations and followed the order MOSQ > MOSMQ > SQ. Electrochemical impedance spectroscopy showed that all compounds act by the formation of a protective film at the metallic surface. The adsorption of three inhibitors on steel surface obeyed Langmuir model, thus the thermodynamic and kinetic parameters were calculated and discussed. In the part based on DFT calculations of this study, some electronic properties of studied molecules were calculated and discussed with the help of B3LYP/6-311G (d,p), B3LYP/6-311 + +G (d,p) and B3LYP/6-311G++ (2d,2p) methods. The theoretical and experimental results are in good agreement.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Acid solutions are generally used for removal of scale from metals, cleaning of boilers and heat exchangers, oil-well acidifying in oil recovery, and so on [1,2]. However, iron and its alloys could be corroded during these applications which result in a waste of resources. So, the search and application for new and efficient corrosion inhibitors become an obligation to prevent corrosion problems. The selection of appropriate inhibitors mainly depends on the structure as well as rational use in various environments. The majority of the well-known inhibitors are organic compounds containing heteroatom, such as O, N and/or S and multiple bonds, which allow an adsorption on the metal surface [3–12]. Many research works have been developed in order to correlate the substituent's effect and the inhibition efficiency of organic molecules [13,14]. Earlier reports [15] have been shown that inhibition efficiency of organic compounds containing heterocyclic nitrogen increases with the number of aromatic rings and the availability of electronegative atoms in their structure.

In the other hand, quantum chemical calculations have been widely used to study reaction mechanisms and to interpret the experimental results as well as to resolve chemical ambiguities [16]. The remarkable inhibition effect is reinforced by the presence of heteroatoms which facilitates its adsorption on metallic surface and follows the sequence O < N < S[17, 18].

Although experimental techniques such as weight loss, potentiodynamic polarization (PDP), Electrochemical impedance spectroscopy (EIS), Fourier transform infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) are very useful to determine the corrosion inhibition efficiencies and to understand the inhibition mechanisms of chemical compounds to be used against corrosion of a metal, they are generally expensive and time-consuming. In recent times, with the improvement of computer hardware and software, computational chemistry programs such as Monte Carlo and Gaussian [19] have become very popular [20]. The efficiency of organic compounds against the corrosion is closely associated with their electronic structure. The electronic structure parameters such as HOMO-LUMO energy gap, chemical hardness, softness, electronegativity, chemical potential, proton affinity, electrophilicity, dipole moment, molecular volume, sum of the total negative charge sum of electronic and zero-point energies can be easily

Corresponding author. E-mail address: azarrouk@gmail.com (A. Zarrouk).

calculated via these mentioned package programs. In addition, it is important to note that Koopman's theorem is very useful in terms of the calculation depending on energies of frontier orbitals of electronic structure parameters mentioned above.

The aim of the present work is to study the inhibition efficiencies of quinoxalinone derivatives on mild steel corrosion in 1.0 M HCl using weight loss measurement, potentiodynamic polarization, electrochemical impedance. Invaluable quantum chemical parameters calculated by DFT at B3LYP/6-311G (d,p), B3LYP/6-311 ++G (d,p) and B3LYP/6-311G + + (2d,2p) levels of the theory help to understand the adsorption properties of studied molecules

2. Experimental details

2.1. Materials

Mild steel containing in wt.%: 0.11 C, 0.24 Si, 0.47 Mn, 0.12 Cr, 0.02 Mo, 0.1 Ni, 0.03 Al, 0.14 Cu, 0.06 W =, <0.0012 Co, <0.003 V and rest Fe was used, and balance iron was used for weight-loss and electrochemical tests. Before each experiment, the mild steel specimen, embedded in Teflon holder using epoxy resin with an exposed area of 1 cm², was used as the working electrode for electrochemical measurements. The coupons and electrodes were abraded with emery paper (up to 1200 grit), cleaned with acetone and washed with distillated water, and finally dried at hot air before being immersed in the acid solution. The aggressive solution was prepared by dilution of an analytical grade HCl solution (37%) with distilled water. The concentration of inhibitors was ranged from 10^{-6} to 10^{-4} M. All assessments were carried out at temperature 25 ± 1 °C.

In the literature, styryl quinoxalines were prepared according to various methods to prepare [21,22]. For our part, we suggested a different synthetic route which comprises reacting fusion 3méthtylquinoxaline-2-one, which was prepared according to Philip's method [23], with aromatic aldehydes. This method, carried out in the absence of solvent, we have a possibility to isolate the desired compound in a yield of around 80%. Indeed, 6.25 mmol of 3méthylquinoxalin-2-one is fused with 12.5 mmol of the appropriate aldehyde for 2 h at the boiling temperature of the latter. At the end of the reaction, the solid compound is allowed to cool and then heated at 100 °C for 10 min in 50 mL of ethanol. The product was filtered hot then was washed with ethanol [4,24]. The ¹H NMR, ¹³C NMR and mass spectroscopy were used to characterize and confirm the obtained product structure. Thus, the characteristics of (E)-3-styrylquinoxalin-2(1H)-one (SO) (Fig. 1), (E)-3-(4-methoxystyryl)quinoxalin-2(1H)-one (MOSQ) (Fig. 2) and (E)-3-(4-methoxystyryl)-7methylquinoxalin-2(1H)-one (MOSMQ) (Fig. 3) are presented in Table 1. These compounds have a low solubility in 1 M HCl solution.

2.2. Electrochemical methods

A saturated calomel electrode (SCE) was used as a reference electrode and all potentials were given with it. The counter electrode was a platinum plate of large surface area.



Fig. 1. (E)-3-styrylquinoxalin-2(1H)-one (SQ).



Fig. 2. (E)-3-(4-methoxystyryl) quinoxalin-2(1H)-one (MOSQ).

In addition, the working electrode was immersed in the test solution during half an hour until a steady state open circuit potential (E_{ocp}) was obtained. The steady-state polarization curves were recorded potentiodynamically using a VoltaLab PGZ 100 and controlled by a personal computer. The cathodic polarization curve was recorded by polarization from E_{ocp} to negative direction under potentiodynamic conditions corresponding to 1 mV s⁻¹ (sweep rate) and under air atmosphere. After this scan, the anodic polarization curve was recorded by polarization from E_{ocp} to positive direction under the same conditions as said before. To extract the corrosion kinetic parameters, the Tafel extrapolation method of the linear part of the cathodic part was used

The corrosion inhibition efficiency is evaluated from the corrosion current densities values using the relationship (3):

$$\eta_{\rm PP} = \frac{i_{\rm corr}^0 - i_{\rm corr}}{i_{\rm corr}^0} \times 100 \tag{3}$$

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

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 Z-View software.

The inhibiting efficiency derived from EIS, η_{EIS} is also added in Table 3 and calculated using the following Eq. (4):

$$\eta_{\rm EIS} = \frac{R_{\rm ct} - R_{\rm ct}^0}{R_{\rm ct}} \times 100 \tag{4}$$

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

2.3. Gravimetric study

Gravimetric experiments were performed according to the standard methods [25], the mild steel sheets of $1 \text{ cm} \times 1 \text{ cm} \times 0.1 \text{ cm}$ were abraded with a series of emery papers (120, 600 and 1200) and then washed with distilled water and acetone. After weighing accurately, the specimens were immersed in a 100 mL beaker containing 250 mL of 1.0 M



Fig. 3. (E)-3-(4-methoxystyryl)-7-methylquinoxalin-2(1H)-one (MOSMQ).

able	1		
------	---	--	--

The characteristics of the synthesized compounds.

Compounds	SQ	MOSQ	MOSMQ
Melting point (°C)	239	260	253
¹ H RMN (300 MHz, DMSO-d6) δ (ppm)	7.29–7.50 (m, 6H, HAr), 7.63 (d, 1H, CH, CH ethylenic, 3 <i>J</i> = 16.5 Hz), 7.73–7.80 (m, 3H, HAr), 8.08 (d, 1H, CH ethylenic, 3 <i>J</i> = 16.5 Hz), 12.48 (s, 1H, NH)	7.45 (s, 1H), 7.50 (d, 2H,3J = 8.4 Hz), 7.60 (d, 1H, CH ethylenic, 3 <i>J</i> = 16.2 Hz), 7.78 (d, 2H, 3J = 8.4 Hz), 8.00 (s, 1H), 8.06 (d, 1H, CH ethylenic, 3 <i>J</i> = 16.2 Hz), 12.64(s, 1H, NH).	7.30–7.35 (m, 2H, HAr), 7.42 (m, 2H, HAr), 7.49–7.57 (m, 2H, HAr), 7.64 (d, 1H, CH ethylenic, $3J = 16.2$ Hz), 7.81 (m, 1H, HAr), 7.98 (m, 1H, HAr), 8.45 (d, 1H, CH ethylenic, $3J = 16.2$ Hz), 12.56 (s, 1H, NH)
¹³ C RMN (75.5 MHz, DMSO-d6) δ (ppm)	115.7, 122.4, 124.0, 128.1, 128.8, 129.0, 129.5, 129.7, 129.9, 130.3, 132.1, 132.8, 136.4, 137.5, 153.5, 155.3	112.55(2 × C), 115.56, 116.63,123.82, 124.05,128.29, 129.27, 129.69 (2 × C), 131.73, 133.09, 138.25, 151.59, 153.96, 155.36.	115.8, 124.1, 125.6, 127.9, 128.3, 129.1, 130.5, 130.7, 131.2, 132.3, 132.6, 132.7, 133.9, 134.2, 153.1, 155.2
The calculate elementary analysis (%)	C 77.40, H 4.87, N 11.28	C 73.37, H 5.07, N 10.07	C 67.97, H 3.92, N 9.91
the percentage founded values	C 77.37, H 4.88, N 11.26	C 73.17, H 5.08, N 10.09	C 67.78, H 3.80, N 9.74
Mass spectroscopy (FAB (MNBA))	m/z (M + H) + = 249	m/z (M + H) + = 279	m/z (M + H) + = 293

HCl solution with and without different inhibitor concentrations. All the aggressive acid solutions were open to air. After 6 h of immersion, the specimens were taken out, washed, dried, and weighed accurately. The inhibition efficiency (η_{WL} %) and surface coverage (θ) were calculated as follows:

$$C_{\rm R} = \frac{W_{\rm b} - W_{\rm a}}{At} \tag{5}$$

$$\eta_{\rm WL}(\%) = \left(1 - \frac{w_{\rm i}}{w_0}\right) \times 100\tag{6}$$

$$\theta = 1 - \frac{w_i}{w_0} \tag{7}$$

where W_b and W_a are the specimen weight before and after immersion in the tested solution, w_0 and w_i are the values of corrosion weight losses of mild steel in uninhibited and inhibited solutions, respectively, *A* the total area of the mild steel specimen (cm²) and *t* is the exposure time (h).

2.4. Computational details and equations

In recent times, DFT methods are widely used the prediction of chemical reactivity of molecules, clusters and solids. All computations have been carried out with the Gaussian package program. For calculations, B3LYP method, a version of the DFT methods, was used and polarized basis sets such as 6-311G (d,p), 6-311++G (d,p), 6-311G++ (2d,2p) were preferred. A full optimization was performed up to a higher basis set denoted by 6-31G++ (d, p) because this basis set gives more accurate results in terms of the determination of geometries and electronic properties for a wide range of organic compounds. The mentioned calculations were performed not only in the gas phase but also in the hydrochloric acid medium. In addition to calculations made for neutral forms of studied compounds, required quantum chemical parameters have been also calculated for the protonated forms of them.

The aim of quantum physicists and chemists is obtain new formulations for calculating of chemical reactivity indices and the understanding of the nature of chemical interactions. Based on the idea that the electron density is the fundamental quantity for describing atomic and molecular properties, Parr and coworkers defined as derivatives of the electronic energy (*E*) with respect to number of electrons (N) at a constant external potential, v(r) the chemical reactivity indices such as chemical potential (μ), electronegativity (χ) and

chemical hardness (η). According to them, mentioned these parameters are given as [26,27]:

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(r)} \tag{8}$$

$$\eta = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_{\upsilon(r)} = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{\upsilon(r)} \tag{9}$$

To calculate the chemical reactivity descriptors such as chemical hardness, chemical potential and electronegativity, Pearson and Parr derived the following equation by applying to Eqs. (8) and (9) [28].

$$\chi = -\mu = \frac{I+A}{2} \tag{10}$$

$$\eta = \frac{I - A}{2} \tag{11}$$

here, *I* and *A* are first vertical ionization energy and electron affinity values of any chemical system, respectively.

Koopman's theorem [29] provides an alternative method the prediction of ionization energy and electron affinities of chemical species. According to this theorem, the negative of the highest occupied molecular orbital energy and the negative of the lowest unoccupied molecular orbital energy corresponds to ionization energy and electron affinity, respectively ($-E_{HOMO} = I$ and $-E_{LUMO} = A$). As a result of this theorem, chemical hardness, electronegativity and chemical potential can be defined as:

$$\mu = -\chi = \frac{E_{LUMO} + E_{HOMO}}{2} \tag{12}$$

$$\eta = \frac{E_{LUM0} - E_{HOM0}}{2} \tag{13}$$

Global softness [30,31] is one of the most important reactivity descriptors. This quantity is defined as the inverse of global hardness and is given as:

$$S = \frac{1}{\eta} = 2\left(\frac{\partial N}{\partial \mu}\right)_{v(r)} \tag{14}$$

Electrophilicity [32] that indicates the tendency of the inhibitor molecule to accept electrons is an important parameter in terms of the comparison of corrosion inhibition efficiencies of molecules. According to electrophilicity index proposed by Parr [33] to explain the electrophilic and nucleophilic behavior of molecules, electrophilic power of a chemical species has been associated with its electronegativity and chemical hardness values. Electrophilicity index introduced by Parr is defined via following equation. It is seen from this equation that a good electrophile is characterized by high electronegativity (or chemical potential) and low chemical hardness values.

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta} \tag{15}$$

3. Results and discussion

3.1. Potentiodynamic polarization curves

Figs. 4, 5 and 6 show the potentiodynamic polarization curves for mild steel in 1.0 M HCl solution in the absence and presence of different concentrations of quinoxalinone derivatives. The i_{corr} , E_{corr} and β_c which were evaluated by the Tafel extrapolation method of the linear part of the cathodic part, were summarized in Table 2. It is seen that all product addition reduces both anodic metal dissolution and cathodic hydrogen evolution reactions. The reduction of i_{corr} is pronounced more and more with increasing inhibitors concentration and MOSQ is the better. The increased inhibition efficiency with inhibitors concentration indicates that the tested compounds act by adsorption on the metallic surface [34]. In addition, it is remarked that the presence of MOSQ and MOSMQ shifts the corrosion potential slightly towards more negative potentials and MS towards positive potentials. Therefore, it is could be classified as the mixed type corrosion inhibitor.

However, the cathodic Tafel slopes (β_c) change with the quinoxalinone substituted compounds addition indicating a modification of the mechanism of cathodic hydrogen evolution, which suggest that these compounds powerfully inhibit the corrosion process of mild steel, and their ability as corrosion inhibitors are enhanced as their concentrations are increased. The suppression of cathodic process can be due to the covering of the surface with monolayer due to the adsorbed inhibitor molecules [35].

In the other hand, the lesser value of inhibition efficiency for MOSMQ as compared to SQ and MOSQ can be attributed to the lower electron densities around the chemisorption center. Compounds can produce protonated species in HCl medium by the reaction of the amino group with HCl. This reaction is easer in case of the presence of $-OCH_3$ (MOSQ) and



Fig. 4. Potentiodynamique polarization curve for mild steel in 1.0 M HCl in the presence of different concentrations of SQ.



Fig. 5. Potentiodynamique polarization curve for mild steel in 1.0 M HCl in the presence of different concentrations of MOSQ.

its absence (SQ) than in the case of presence of $-OCH_3$ with $-CH_3$. The better performance of MOSQ over SQ and MOSMQ is also due to the more surface area which leads to more adsorption on the metal surface, thereby exhibiting a better inhibitory effect.

3.2. Electrochemical impedance spectroscopy (EIS)

The representative Nyquist of mild steel electrode in 1.0 M HCl solution in the absence and presence of various concentrations of SQ, MOSQ and MOSMQ at corrosion potential is shown in Figs. 7, 8 and 9. It is noted that the Nyquist plot of mild steel in the absence and presence of all concentration of inhibitors 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. 10, with one time constants was proposed to reproduce these results by non linear regression calculation. Excellent fit with this model was obtained for all experimental data. As an example, the Nyquist and Bode plots for mild steel in acid solution in the presence of 10^{-4} of MOSQ is presented in Fig. 11a, b and c, respectively. The measured and simulated data fitted very well. It is observed that the fitted data follow almost the same pattern as the original results along the whole diagrams. The high



Fig. 6. Potentiodynamique polarization curve for mild steel in 1.0 M HCl in the presence of different concentrations of MOSMQ.

Table 2

Potentiodynamic electrochemical parameters obtained for mild steel in 1.0 M HCl containing different concentrations of quinoxalinone substituted compounds.

Inhibitors	Conc. (M)	$E_{\rm corr}$ (mV/SCE)	i _{corr} (mA cm ⁻²)	$\frac{-\beta_c}{(mVdec^{-1})}$	$\eta_{ m PP}$ (%)
1.0 M HCl	00	- 545	0.949	- 101	_
SQ	1×10^{-6}	-436	0.130	- 143	86
	$1 imes 10^{-5}$	-448	0.126	- 145	87
	$5 imes 10^{-5}$	-508	0.116	-121	88
	1×10^{-4}	-488	0.112	-145	88
MOSQ	$1 imes 10^{-6}$	-596	0.197	-120	79
	1×10^{-5}	-594	0.169	- 121	82
	5×10^{-5}	-628	0.109	-102	89
	1×10^{-4}	-680	0.083	-144	91
MOSMQ	1×10^{-6}	-594	0.875	-148	07
	1×10^{-5}	-594	0.248	-113	74
	5×10^{-5}	-628	0.148	-114	84
	1×10^{-4}	-628	0.096	-113	90

frequency part of the impedance and phase angle describes the behavior of an inhomogeneous surface layer, while the low frequency contribution shows the kinetic response for the charge transfer reaction [36].

It is worth pointing out that the application of an electrical circuit consisting of double layer capacitor does not always enable achieving satisfactory fitting to the experimental impedance data. The dispersion of the impedance data can be attributed to the surface heterogeneity resulting from the inhibitor's adsorption (mainly), surface roughness, dislocations, impurities, grain boundaries, fractality, etc. In such case using an equivalent electrical circuit employing the double layer capacitance element is not a good enough approximation. The Constant Phase Element (*CPE*) was suggested instead of C_{dl} . So, the more heterogeneous surface, hence the higher *n* values, the greater deviation from ideal capacitative behavior. It allows employing *CPE* element in order to investigate the inhibitive film properties on metallic surface. Thus, the impedance of the *CPE* can be described by the following equation:

$$Z_{\rm CPE} = \left[Q(j\omega)^n \right]^{-1} \tag{16}$$

where *j* is the imaginary number, *Q* is the frequency independent real constant, $\omega = 2\pi f$ is the angular frequency (rad s⁻¹), *f* is the frequency of the applied signal, *n* is the *CPE* exponent for whole number of n = 1, 0, -1, *CPE* is reduced to the classical lump element-capacitor (*C*), resistance (*R*) and inductance (*L*) [37]. The use of these parameters, similar to the constant phase element (*CPE*), allowed the depressed feature of Nyquist plot to be reproduced readily. However, the calculated double



Fig. 7. Nyquist plots for mild steel in 1.0 M HCl in the presence of different concentrations of SQ at corrosion potential.



Fig. 8. Nyquist plots for mild steel in 1.0 M HCl in the presence of different concentrations of MOSQ at corrosion potential.

layer capacitance (C_{dl}) derived from the CPE parameters according to the equation [38]:

$$C_{dl} = \left(\mathsf{Q}_{dl} \mathsf{R}_{ct}^{1-n} \right)^{1/n}$$

and the relaxation time constant (τ_d) of charge-transfer process using the equation [38]:

$$\tau_{\rm d} = C_{\rm dl} R_{\rm ct}$$

The most important data obtained from the equivalent circuit are presented in Table 3. It is apparent from this Table that the impedance of the inhibited system amplified with increasing inhibitors concentration and the $C_{\rm dl}$ values decreased with increasing inhibitors concentrations. This decrease in $C_{\rm dl}$ results from a decrease in local dielectric constant and/or an increase in the thickness of the double layer, suggesting that inhibitors molecules inhibit the mild steel corrosion by adsorption at the metal/acid interface [39].

In addition, it is shown that the *n* values increase with inhibitors concentrations, which could be related to the decrease of the surface heterogeneity as a result of the inhibitors molecules adsorption on mild



Fig. 9. Nyquist plots for mild steel in 1.0 M HCl in the presence of different concentrations of MOSMQ at corrosion potential.



Fig. 10. The electrochemical equivalent circuit used to fit the impedance measurements that include a solution resistance (R_s), a constant phase element (CPE) and charge transfer resistance (R_{ct}).

steel surface and forming a uniform inhibitive film. In the same way, the relaxation time constant ($\tau_{\rm dl}$) values increase with inhibitors concentrations as well and the time of adsorption process becomes therefore much higher which means a slow adsorption process [40]. This shows that there is an agreement between the amount of charge that can be stored (that is capacitance) and discharge velocity in the interface ($\tau_{\rm dl}$) [41].

In addition, the charge transfer resistance of the material followed the order MOSQ > MOSMQ > SQ such as found by the potentiodynamic polarization curves.

3.3. Gravimetric study

3.3.1. Effect of inhibitor concentration and temperature

Corrosion parameters, namely C_R , surface coverage (θ), and inhibition efficiency (η_{WL} %) of mild steel in 1.0 M HCl solution in the absence and presence of different concentrations

 $(10^{-6}-10^{-4}$ M) of inhibitor at different temperatures (298 – 328 K), obtained from weight loss measurements are shown in Table 4. From Table 4, it is apparent that inhibition efficiency increased by increasing the concentration of the inhibitors. The inhibition efficiency of MOSQ, SQ and MOSMQ at 10^{-4} M was found to be 89, 88 and 83%, respectively, at 298 K (Table 4). By increasing the inhibitor concentration, the part of metal surface covered by inhibitor molecules increases, and that leads to an increase in the inhibition efficiencies [42]. It is also clear from the Table 4 that the inhibition efficiency decreased with increasing temperature from 298 to 328 K. Such type of behavior can be described on the basis that the increase in temperature leads to a shift of the equilibrium constant toward desorption of the inhibitors molecules at the surface of mild steel [43].

3.3.2. Activation parameters

The effect of temperature on the corrosion parameters of mild steel in free acid and inhibited 1.0 M HCl solution was studied in the temperature range of 298–328 K. The effect of temperature on inhibition reaction is highly complex, because many changes may occur on the metal surface such as etching, rupture and desorption of inhibitor molecules. The dependence of logarithm of corrosion rates ($Ln C_R$) on the reciprocal of absolute temperature (1/T) for 1.0 M HCl for blank and quinoxalines derivatives was examined. Linear plots were obtained (Fig. 12), which indicate it follows Arrhenius equation [44].

$$LnC_R = -\frac{E_a}{RT} + LnA \tag{17}$$



Fig. 11. (a) Nyquist plots, (b) Bode-Model and (c) Bode-phase plots obtained for the mild steel in 1.0 M HCl in the presence of 10^{-4} of MOSQ. Scatters: Experimental data and red lines: Fitting data. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 3			
Fitting results of EIS for mild steel in 1.0 M HCl in the absence and	presence of different concentrations of o	quinoxalinone substituted co	mpounds.

Inhibitors	С	Rs	R _{ct}	C _{dl}	$ au_{ m ct}$	n _{ct}	η_{EIS}
	(M)	$(\Omega \text{ cm}^2)$	$(\Omega \text{ cm}^2)$	$(\mu F \text{ cm}^{-2})$	(s)		(%)
1.0 M HCl	00	2.08 ± 0.03	32.41 ± 0.78	128.1 ± 0.66	0.0041	0.78 ± 0.01	-
SQ	1×10^{-6}	1.61 ± 0.05	222.70 ± 3.87	108.10 ± 1.31	0.0241	0.84 ± 0.01	85
	1×10^{-5}	1.42 ± 0.03	258.60 ± 2.56	75.85 ± 0.31	0.0196	0.83 ± 0.03	87
	5×10^{-5}	1.35 ± 0.07	280.00 ± 2.63	59.40 ± 0.71	0.0166	0.82 ± 0.01	88
	1×10^{-4}	1.30 ± 0.03	385.90 ± 19.67	65.03 ± 0.64	0.0251	0.85 ± 0.01	92
MOSQ	1×10^{-6}	1.97 ± 0.01	144.90 ± 0.39	94.46 ± 0.15	0.0137	0.86 ± 0.001	78
	1×10^{-5}	1.96 ± 0.01	166.40 ± 0.43	73.48 ± 0.08	0.0122	0.84 ± 0.001	81
	5×10^{-5}	1.69 ± 0.01	223.70 ± 1.02	90.24 ± 0.31	0.0201	0.88 ± 0.001	86
	1×10^{-4}	2.05 ± 0.02	520.20 ± 1.96	53.43 ± 0.08	0.0278	0.85 ± 0.001	94
MOSMQ	1×10^{-6}	2.163 ± 0.02	34.29 ± 0.36	119.45 ± 2.35	0.0041	0.85 ± 0.002	06
	1×10^{-5}	4.65 ± 0.06	150.00 ± 0.84	77.60 ± 0.07	0.0116	0.76 ± 0.01	78
	5×10^{-5}	1.914 ± 0.02	236.60 ± 2.13	95.50 ± 0.49	0.0226	0.84 ± 0.03	86
	1×10^{-4}	2.109 ± 0.01	402.00 ± 1.40	80.93 ± 0.12	0.0325	0.86 ± 0.001	92

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 5.

All the linear regression coefficients are close to 1, indicating that the steel corrosion in hydrochloric acid can be elucidated using the kinetic model. As observed from the Table 5, the E_a increased with increasing concentration of quinxaline derivatives, but all values of E_a in the range of the studied concentration, were higher than that of the uninhibited solution (Blank). The increase in E_a in the presence of quinoxaline derivatives may be interpreted as physical adsorption. Indeed, a higher energy barrier for the corrosion process in the inhibited solution is associated with physical adsorption or weak chemical bonding between the inhibitors species and the steel surface [45,46]. Szauer et al. explained that the increase in activation energy can be attributed to an appreciable decrease in the adsorption of the inhibitor on the mild steel surface with the increase in temperature [47].

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

$$C_R = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(-\frac{\Delta H_a}{RT}\right)$$
(18)

where C_R is the corrosion rate, *h* the Plank's constant and *N* is Avogrado's number, ΔH_a the enthalpy of activation and ΔS_a the entropy of activation.

Fig. 13 shows the variation of Ln (C_R/T) function (1/T) as a straight line with a slope of $(-\Delta H_a/R)$ and the intersection with the y-axis is $[Ln(R/Nh) + (\Delta S_a/R)]$. From these relationships, values of ΔS_a and ΔH_a can be calculated. The activation parameters (E_a , ΔH_a and ΔS_a) calculated from the slopes of Arrhenius lines in the absence and presence of our inhibitors (Figs. 12 and 13) are summarized in Table 5.

Inspection of these data reveals that the ΔH_a values for dissolution reaction of mild steel in 1.0 M HCl in the presence of three quinxaline derivatives are higher than that of in the absence of inhibitors (59.15 kJ mol⁻¹). The positive signs of ΔH_a values reflect the endothermic nature of the mild steel dissolution process suggesting that the dissolution of mild steel is slow [37] in the presence of inhibitor. All values of E_a are larger than the analogous values of ΔH_a indicating that the corrosion process must involved a gaseous reaction, simply the hydrogen evolution reaction, associated with a decrease in the total reaction volume [48].

Additionally, Table 5 shows that the values of ΔS_a increase in presence of inhibitor compared to blank solution, which mean an increase in disorder takes place during the course of the transition from reactant to the activated complex during the corrosion process [49,50].

3.3.3. Adsorption isotherm and thermodynamic analysis

The mode and extent of the interaction between an inhibitor and the mild steel surface can be studied by applying adsorption isotherms. The degree of surface coverage, θ , at different inhibitor concentrations of

Table 4

Corrosion parameters of mild steel in 1.0 M HCl solution in the presence and absence of different inhibitors at different temperature, obtained from weight loss measurements.

	298 K			298 K 308 K				318 K			328 K		
Conc (M)	$C_{\rm R}$ (mg/cm ² h)	θ	η _{WL} (%)	$C_{\rm R}$ (mg/cm ² h)	θ	η _{WL} (%)	$C_{\rm R}$ (mg/cm ² h)	θ	η_{WL} (%)	$C_{\rm R}$ (mg/cm ² h)	θ	η_{WL} (%)	
Blank MOSQ	1.310	_	_	1.860	_	_	2.970	_	-	4.560	_	-	
1×10^{-6}	0.390	0.70	70	0.591	0.68	68	1.060	0.64	64	1.808	0.60	60	
1×10^{-5}	0.338	0.74	74	0.518	0.72	72	0.906	0.70	70	1.618	0.65	65	
$5 imes 10^{-5}$	0.261	0.80	80	0.443	0.76	76	0.843	0.72	72	1.476	0.68	68	
$1 imes 10^{-4}$	0.138	0.89	89	0.272	0.85	85	0.551	0.82	82	1.028	0.78	78	
SQ													
1×10^{-6}	0.254	0.81	81	0.406	0.78	78	0.769	0.74	74	1.368	0.70	70	
1×10^{-5}	0.213	0.84	84	0.350	0.81	81	0.679	0.77	77	1.222	0.73	73	
$5 imes 10^{-5}$	0.195	0.85	85	0.309	0.83	83	0.649	0.78	78	1.081	0.76	76	
1×10^{-4}	0.160	0.88	88	0.273	0.85	85	0.579	0.81	81	0.998	0.78	78	
MOSMQ													
1×10^{-6}	1.189	0.09	09	1.724	0.07	07	2.778	0.06	06	4.317	0.05	05	
1×10^{-5}	0.642	0.51	51	1.084	0.42	42	1.864	0.37	37	3.002	0.34	34	
$5 imes 10^{-5}$	0.372	0.72	72	0.583	0.69	69	1.037	0.65	65	1.739	0.62	62	
$1 imes 10^{-4}$	0.267	0.80	80	0.460	0.75	75	0.828	0.72	72	1.398	0.69	69	



Fig. 12. Arrhenius plots for mild steel in 1.0 M HCl solution in the absence and presence of various concentrations of SQ, MOSQ and MOSMQ.

MOSQ, SQ and MOSMQ in 1.0 M HCl was evaluated from weight loss measurements to explain the best isotherm to determine the adsorption process. The linear relationship between θ values and C_{inh} is to be found in order to obtain the isotherm. Attempts were made to fit the θ values to various isotherms including Langmuir, Temkin, Frumkin, and Flory-

Table 5

Activation parameters for mild steel corrosion in 1.0 M HCl in the absence and presence of different concentrations of quinoxalinone derivatives.

Inhibitor	C (M)	E _a (KJ/mol)	ΔH_a (KJ/mol)	$\Delta S_a (J/(mol K))$
	0.0	34.17	31.55	-137.09
MOSQ	1×10^{-6} 1×10^{-5} 5×10^{-5}	42.10 46.61 47.49	39.48 39.99 44.86	- 120.71 - 120.20 - 105.83
SQ	1×10^{-4} 1×10^{-6} 1×10^{-5} 5×10^{-5} 1×10^{-4}	54.69 46.18 47.95 47.74 50.77	52.05 43.48 45.32 45.11 48.13	- 86.78 - 110.84 - 106.12 - 107.57 - 98.96
MOSMQ	$\begin{array}{c} 1\times 10^{-6} \\ 1\times 10^{-5} \\ 5\times 10^{-5} \\ 1\times 10^{-4} \end{array}$	35.24 42.01 42.24 45.15	33.62 35.28 38.33 43.96	- 131.28 - 130.45 - 122.29 - 110.03

Huggins. The best fit is obtained with the Langmuir isotherm. The Langmuir adsorption isotherm is given by [51]

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{19}$$

where C_{inh} is the equilibrium inhibitor concentration, K_{ads} adsorptive equilibrium constant.

A plot of C_{inh}/θ against C_{inh} shows a straight line, indicating that adsorption follows the Langmuir adsorption isotherm as shown in Fig. 14.

Thermodynamic parameters including the heat of adsorption, free energy of adsorption, and entropy of adsorption are important in the explanation of the corrosion inhibition mechanism. The free energy of adsorption (ΔG_{ads}) can be obtained from the equation [52]

$$\Delta G_{ads} = -RTLn(55.5K_{ads}) \tag{20}$$

where *R* is gas constant and *T* is absolute temperature of experiment and the constant value of 55.5 is the concentration of water in solution in mol L^{-1} .

The enthalpy and entropy of adsorption (ΔH_{ads} and ΔS_{ads}) can be calculated using the following equations [53]:

$$\Delta G_{ads} = \Delta H_{ads} - T \Delta S_{ads} \tag{21}$$

$$LnK_{ads} = -\frac{\Delta H_{ads}}{RT} + \frac{\Delta S_{ads}}{R} - Ln(55.5)$$
(22)

Fig. 15 represents the plots of Ln K_{ads} versus 1/T for MOSQ, SQ and MOSMQ, and the thermodynamic parameters obtained are given in Table 6.

The values of ΔG_{ads} are negatives the stability of the adsorbed layer on the steel surface. Generally speaking, the adsorption type is regarded as physisorption if the absolute value of ΔG_{ads} was of the order of 20 kJ mol⁻¹ or lower. The inhibition behavior is attributed to the electrostatic interaction between the organic molecules and iron atom. When the absolute value of ΔG_{ads} is of the order of 40 kJ mol⁻¹ or higher, the adsorption could be seen as chemisorption. In this process, the covalent bond is formed by the charge sharing or transferring from the inhibitor molecules to the metal surface [54,55]. Based on the literature [56], the calculated ΔG_{ads} values in this work (Table 6) indicate that the adsorption mechanism of these compounds on mild steel in 1.0 M HCl solution is typical of chemisorption. The same conclusion was given by Wang et al. [57] concerning the interaction of mild steel with mercapto-triazoles and 5-amino-3-mercapto-1,2,4-triazole, respectively. Moreover, $|\Delta G_{ads}|$ of these inhibitors decreases in the order SQ > MOSQ > MOSMQ.

 ΔH_{ads} is another criterion from which the mode of adsorption based on the absolute value can be probed. Generally, an endothermic process





Fig. 13. Transition Arrhenius plots for mild steel in 1.0 M HCl solution in the absence and presence of various concentrations of SQ, MOSQ and MOSMQ.

Fig. 14. Langmuir adsorption isotherm of mild steel 1.0 M HCl containing various concentrations of MOSQ, SQ and MOSMQ.

is explicit to chemisorption, while an exothermic adsorption process designates either physisorption or chemisorption [58]. In an exothermic adsorption, the adsorption mode is judged based on the absolute value of ΔH_{ads} . The negative sign of ΔH_{ads} indicates that the adsorption of

inhibitor molecules is an exothermic process. ΔS_{ads} in the presence of these inhibitors is large and positive meaning that an increase in disordering takes places in going from reactants to the metal adsorbed species reaction complex [57]. The value of the constant K_{ads} decreases with increasing temperature, indicating that the interactions between



Fig. 15. The relationship between Ln (K_{ads}) and 1000/T for MOSQ, SQ and MOSMQ.

the adsorbed molecules and the metal surface are weakened and, consequently, the adsorbed molecules become easily removable.

3.4. Quantum chemical calculations

To compare more easily the quantum chemical parameters such as dipole moment, total negative charge, electronegativity, chemical potential, hardness, softness, global electrophilicity, molecular volume and sum of electronic and zero point energies calculated for studied compounds using B3LYP/6-311G(d,p), B3LYP/6-311++G(d,p) and B3LYP/6-311++G(2d,2p) methods in both gas phase and solvent phase, the results obtained are presented as column graphs in Fig. 16. In addition, Fig. 14 presents the optimized molecular structure, HOMOs, LUMOs and molecular electrostatic potential maps of protonated and neutral forms of studied molecules. In the Table 7, calculated HOMO, LUMO energies and energy gap (ΔE) values are presented. In this stage, we should provide descriptive information about labeling in Figs. 16 and 17. For example, SQ-prot-N label symbolizes that molecule SQ has been protonated via oxygen atom.

Corrosion inhibition efficiencies of molecules are closely associated with their reactivities or stabilities. The calculated quantum chemical parameters such as the highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), the energy gap between E_{HOMO} and E_{LUMO} (ΔE), dipole moments (DM),

Table 6 Thermodynamic and kinetic parameters for the adsorption of studied inhibitors in 1.0 M HCl on the mild steel surface at different temperatures.

Inhibitors	Temp (K)	K_{ads} (L mol ⁻¹)	ΔG_{ads} (KJ mol ⁻¹)	ΔH_{ads} (KJ mol ⁻¹)	ΔS_{ads} (J mol ⁻¹ K ⁻¹)
MOSQ	298	425126.69	-42.06	-7.58	115.70
	318	372160.88	-43.42 -44.53	-7.58	116.19
	328	322704.52	-45.54	-7.58	115.73
SQ	298	1502437.70	-45.19	-6.38	130.23
	308	1730292.40	-47.07	-6.38	132.11
	318	1268119.85	-47.77	-6.38	130.16
	328	1278404.55	-49.30	-6.38	130.85
MOSMQ	298	105349.10	-38.60	- 16.76	73.29
	308	80894.37	-39.22	-16.76	72.92
	318	66441.21	-39.98	-16.76	73.02
	328	56676.17	-40.80	-16.76	73.29

molecular volume (MV), sum of the total negative charge (TNC), global hardness (η), softness (σ), chemical potential (μ), electronegativity (χ), global Electrophilicity (ω) and sum of electronic and zero-point energies (SEZPE) are important and useful tools to compare the corrosion inhibition performances of molecules [59–65].

In the estimation of the strength of the intermolecular interactions, energy levels of HOMO and LUMO orbitals have an important role. In DFT studies, in general, molecular reactivities of molecules are investigated via the analysis of frontier molecular orbital [66]. The energy of HOMO is associated with the electron donating ability of a molecule. High values of energy of HOMO state that the molecule is prone to donate electrons to appropriate acceptor molecules with low energy and empty molecular orbital. On the other hand, LUMO energy level is an indicator of electron accepting abilities of molecules. It is important to note that the molecules that have lower LUMO energy value have more electron accepting ability. Calculated HOMO and LUMO energies for neutral forms of studied guinoxalinone derivatives are presented in Fig. 16. According the results obtained in gas phase, molecule MOSO can be considered as a better corrosion inhibitor compared to other molecules. However, the results obtained in solvent phase show that molecule MOSMQ acts a corrosion inhibitor better than molecule MOSQ in acidic medium. As a result, in terms of the energies of frontier orbitals, corrosion inhibition efficiency ranking of studied molecules can be given as: MOSO > MOSMO > SO. This result is in good agreement with the experimental data.

There are many quantum chemical parameters which are used reactivity descriptors in chemical reactions. One of these parameters is chemical hardness which is defined as the resistance towards electron cloud polarization and deformation of chemical species [67,68]. Hard and Soft Acids-Bases (HSAB) [69] and Maximum Hardness (MHP) [27] Principles based on chemical hardness concept are very useful in terms of estimating the directions of chemical reactions and understanding of the nature of chemical interactions. According to Maximum Hardness Principle, a chemical system tends to arrange itself so as to achieve maximum hardness and chemical hardness can be considered as a measure of stability. As can be understood from this information, a good corrosion inhibitor is characterized by low chemical hardness value. According to calculated hardness values given in the corresponding figure, the corrosion inhibition efficiency ranking of studied molecules can be given as: MOSO \approx MOSMO > SO in gas phase and MOSQ > MOSMQ > SQ in solvent phase. As mentioned above, softness is the inverse of chemical hardness and it is a measure of polarizability and reactivity. Soft molecules are more reactive and more effective against corrosion. A comparison among the studied compound shows that the trend of increasing softness values is as follows: $MOSQ \approx MOSMQ > SQ$ in gas phase and MOSQ > MOSMQ > SQ in solvent phase. The trend is consistent with the trend in the experimental inhibition efficiencies. Chemical hardness, softness and energy gap (ΔE) quantum chemical parameters closely associated with each other. It is known that both softness and hardness are given based on HOMO and LUMO orbital energies as a result of Koopman's theorem. Hard molecules which have high HOMO-LUMO energy gap cannot act as good corrosion inhibitor. However, soft molecules which have low HOMO-LUMO energy gap are good corrosion inhibitors because they can easily give to metals. It is important to note that an efficient inhibitor is characterized by a small energy gap. The order in which energy gap values change is also consistent with the experimental data.

Electronegativity [70] is a key parameter that determines the fraction of electrons transferred (ΔN) from inhibitor molecule to metal surface [71]. Chemical potential is the negative of the electronegativity. It is seen from the equation given below that the electron transfer value metal and inhibitor decreases as the electronegativity of inhibitor increases. According to Sanderson's electronegativity equalization principle, the electron transfer between metal and inhibitor continues until their electronegativity values become equal with each other. According





Fig. 16. The calculated quantum chemical parameters for the non-protonated for gas and solvent phase compounds using B3LYP/6-311G(d,p), B3LYP/6-311++G(d,p) and B3LYP/6-31++G(d,p) and B3LYP/6-31





to Pearson, the fraction of electrons transferred from corrosion inhibitor to metal atom can be calculated via following equation.

$$\Delta N = \frac{\chi_M - \chi_{inh}}{2(\eta_M + \eta_{inh})}$$
(23)

where, ΔN is electron transfer between metal and inhibitor. χ_M and χ_{inh} are electronegativity of metal and electronegativity of inhibitor, respectively. η_M and η_{inh} represent chemical hardness value of metal and chemical hardness value of inhibitor, respectively. In terms of the electronegativity and chemical potential values of inhibitor molecules, the corrosion inhibition efficiencies follow the order: MOSQ \approx MOSMQ > SQ.

Electrophilicity is a useful tool to predict of chemical behaviors of molecules and this quantity can be used to compare the tendency of the inhibitor molecule to accept the electrons [72]. For this reason, it should be stated that a molecule that has large electrophilicity value is ineffective against corrosion. The trend in which the electrophilicity values increases is as follows: SQ > MOSMQ > MOSQ. Within framework of this information, we can write the corrosion inhibition efficiency ranking of the molecules as: MOSQ > MOSMQ > SQ. This ranking is compatible with the experimental inhibition efficiency ranking.

Proton affinity [73] is a measure of basicity and it can be defined as the enthalpy of the reaction with H⁺ ion of a chemical species in gas phase. As can be understood from this definition, comparisons regarding proton affinities of molecules should be performed considering the results obtained in the gas phase. Organic compounds containing





heteroatoms such as oxygen, sulfur and nitrogen exhibit high tendency to protonation in acidic medium. Thus, analysis of the protonated forms of studied compounds is important in terms of the calculation of the proton affinities of neutral inhibitors. In Fig. 16, calculated quantum chemical parameters for protonated forms of considered molecules in this study are presented. To determine the most appropriate heteroatom for protonation, studied quinoxalin derivatives have been protonated from different regions. It should be noted that a chemical compound with high proton affinity acts as a good corrosion inhibitor. If so, according to proton affinity values given in Fig. 16 of studied compounds, corrosion inhibition efficiencies follow the order: MOSQ > MOSMQ > SQ. Proton affinity values obtained have been calculated considering Eqs. (24) and (25):

$$PA = E_{(pro)} - (E_{(non-pro)} + E_{H^+})$$
(24)

where, $E_{\text{non-pro}}$ and E_{pro} are the energies of the non-protonated and protonated inhibitors, respectively. E_H^+ is the energy of H⁺ ion and was calculated as:

$$E_{\rm H^+} = E_{\rm (H_3O^+)} - E_{\rm (H_2O)}$$
(25)

The molar volumes of inhibitor molecules can be provide an alternative insight to compare their inhibition efficiencies [74]. The inhibition efficiency increases as the molecular volume increases because of the increase of the contact area between inhibitor molecule and metal surface. It is seen from the Fig. 16, in general, molecule MOSMQ has the highest molecular volume values. This condition is not consistent with the experimental results. In the solvent phase, only the corrosion inhibition efficiency ranking obtained using B3LYP/6-311 + +G (d.p) is in agreement with experimental results. Another important electronic parameter considered in corrosion studies is dipole moment. The dipole moment arises from non-uniform distribution of charges on the various atoms in a molecule and is used in the estimation of strength of intermolecular interactions. Some authors reported that the inhibition efficiency increases with increasing value of the dipole moment. On the other hand some authors also reported that irregularities can be observed in the correlation between dipole moment with inhibition efficiency. Inhibition efficiency ranking obtained in the theoretical part of our study is not compatible with the experimental results. It is seen from dipole moment values given in Fig. 16, for molecules SQ, MOSQ and MOSMQ, there was no obvious correlation between the values of



Fig. 17. The optimized molecular structures, HOMO, LUMO and total density of the gas phase and gas phase with protonated inhibitor molecules using DFT/B3LYP/6-311++G(2d,2p).



Fig. 17 (continued).

the dipole moment with the trend of inhibition efficiency obtained experimentally. Another parameter also considered in corrosion studies is total negative charge (TNC). It should be noted that TNC is not very useful parameter to compare the electron donating abilities of molecules. Nevertheless, in some publications, it was expressed that a molecule having high TNC value can be very effective against corrosion. the most effective corrosion inhibitor for prevention of corrosion of mild steel in acidic medium among studied molecules is molecule MOSQ and the corrosion inhibition efficiency ranking obtained as theoretical is MOSQ > MOSMQ > SQ.

4. Conclusion

As to conclude, the results obtained quantum chemical calculations are generally compatible with experimental results. Considering the results obtained in the theoretical section of this study, we propose that

The corrosion inhibition of mild steel in 1.0 M HCl solution by new quinoxalinone derivatives was investigated using electrochemical

-

Table 7

The calculated HOMO, LUMO and Energy Gap (ΔE) parameters as eV for the non-protonated and protonated for gas and solvent phase compounds using B3LYP/6-311G(d,p), B3LYP/6-311++G(d,p) and B3LYP/6-11++G(d,p) methods.

Method									
Molecule	B3LYP/6-3110	G(d,p)		B3LYP/6-311	++G(d,p)		B3LYP/6-311	++G(2d,2p)	
	E _{HOMO}	E _{LUMO}	ΔE	E _{HOMO}	E _{LUMO}	ΔE	E _{HOMO}	E _{LUMO}	ΔE
Gas phase for non-protor	nated molecules								
SQ	-5.994	-2.364	3.629	-6.021	-2.563	3.457	-6.006	-2.549	3.457
MOSQ	-5.675	-2.243	3.432	-5.688	-2.411	3.277	-5.671	-2.390	3.281
MOSMQ	-5.594	-2.317	3.278	-5.594	-2.317	3.278	-5.576	-2.295	3.281
Solvent phase for non-pr	otonated molecule.	S							
SQ	-5.946	-2.460	3.486	-6.048	-2.587	3.461	-6.024	-2.576	3.448
MOSQ	-5.759	-2.464	3.295	-5.794	-2.515	3.279	-5.831	-2.580	3.251
MOSMQ	- 5.634	-2.333	3.301	- 5.736	-2.459	3.278	-5.713	-2.447	3.265
Gas phase for protonated	molecules								
SQ-Prot-N	-9.745	-6.935	2.811	-9.780	-6.967	2.813	-9.748	-6.937	2.810
MOSQ-Prot-N	-9.168	-6.639	2.528	-9.213	-6.604	2.609	-9.184	-6.569	2.615
MOSMQ-Prot-N	-9.049	-6.531	2.518	-9.125	-6.622	2.503	-9.052	-6.473	2.579
SQ-Prot-N-O	- 12.916	-10.917	1.999	-12.979	-11.014	1.966	- 12.961	-10.981	1.980
MOSQ-Prot-N-O	- 12.189	-10.495	1.694	-12.267	-10.321	1.946	-12.243	-10.289	1.954
MOSMQ-Prot-N-O	- 12.018	- 10.373	1.644	-12.064	- 10.197	1.867	-12.045	-10.167	1.878
SQ-Prot-O	-9.114	-6.539	2.575	-9.186	- 6.735	2.451	-9.184	-6.699	2.485
MOSQ-Prot-O	-8.504	-6.339	2.165	-8.564	-6.496	2.068	-8.564	-6.455	2.109
MOSMQ-Prot-O	-8.409	- 6.256	2.153	- 8.455	-6.372	2.084	-8.445	-6.326	2.119
Solvent phase for protono	ated molecules								
SQ-Prot-N	-9.748	-6.937	2.810	-6.819	- 3.893	2.925	-6.822	-3.865	2.957
MOSQ-Prot-N	-9.184	-6.569	2.615	-6.438	-3.740	2.697	-6.411	-3.713	2.699
MOSMQ-Prot-N	-9.052	-6.473	2.579	-6.374	-3.707	2.666	-6.336	-3.664	2.673
SQ-Prot-N-O	-12.961	-10.981	1.980	-7.251	-4.699	2.552	-7.220	-4.667	2.553
MOSQ-Prot-N-O	-12.243	-10.289	1.954	-6.766	-4.505	2.262	-6.741	-4.477	2.264
MOSMQ-Prot-N-O	-12.045	-10.167	1.878	-6.692	-4.477	2.214	-6.663	-4.436	2.227
SQ-Prot-O	-9.184	-6.699	2.485	-6.587	-3.512	3.075	-6.566	-3.482	3.084
MOSQ-Prot-O	-8.564	-6.455	2.109	-6.157	- 3.442	2.716	-6.138	-3.412	2.726
MOSMQ-Prot-O	- 8.445	-6.326	2.119	-6.115	-3.376	2.739	-6.090	-3.332	2.758
Gas phase for non-protor	nated molecules								
SQ	-5.994	-2.364	3.629	-6.021	-2.563	3.457	-6.006	-2.549	3.457
MOSQ	- 5.675	-2.243	3.432	-5.688	-2.411	3.277	-5.671	-2.390	3.281
MOSMQ	-5.594	-2.317	3.278	-5.594	-2.317	3.278	-5.576	-2.295	3.281
Solvent phase for non-pro	otonated molecule.	S							
SQ	-5.946	-2.460	3.486	-6.048	-2.587	3.461	-6.024	-2.576	3.448
MOSQ	-5.759	-2.464	3.295	-5.794	-2.515	3.279	-5.831	-2.580	3.251
MOSMQ	-5.634	-2.333	3.301	-5.736	-2.459	3.278	-5.713	-2.447	3.265
Gas phase for protonated	molecules								
SQ-Prot-N	-9.745	-6.935	2.811	-9.780	-6.967	2.813	-9.748	-6.937	2.810
MOSQ-Prot-N	-9.168	- 6.639	2.528	-9.213	-6.604	2.609	-9.184	-6.569	2.615
MOSMQ-Prot-N	-9.049	-6.531	2.518	-9.125	-6.622	2.503	-9.052	-6.473	2.579
SQ-Prot-N-O	- 12.916	- 10.917	1.999	-12.979	-11.014	1.966	-12.961	-10.981	1.980
MOSQ-Prot-N-O	- 12.189	- 10.495	1.694	-12.267	-10.321	1.946	-12.243	-10.289	1.954
MOSMQ-Prot-N-O	- 12.018	- 10.373	1.644	-12.064	-10.197	1.867	-12.045	-10.167	1.878
SQ-Prot-O	-9.114	-6.539	2.575	-9.186	-6.735	2.451	-9.184	-6.699	2.485
MOSQ-Prot-O	- 8.504	-6.339	2.165	- 8.564	-6.496	2.068	-8.564	-6.455	2.109
MOSMQ-Prot-O	- 8.409	- 6.256	2.153	- 8.455	-6.372	2.084	- 8.445	-6.326	2.119
Solvent phase for protono	ated molecules					0.4			
SQ-Prot-N	-9.748	-6.937	2.810	-6.819	- 3.893	2.925	-6.822	- 3.865	2.957
MUSQ-Prot-N	-9.184	- 6.569	2.615	-6.438	- 3.740	2.697	-6.411	-3.713	2.699
MUSMQ-Prot-N	- 9.052	- 6.473	2.579	-6.374	- 3.707	2.666	-6.336	-3.664	2.673
SQ-Prot-N-O	- 12.961	- 10.981	1.980	- 7.251	-4.699	2.552	-7.220	-4.667	2.553
MUSQ-Prot-N-O	- 12.243	- 10.289	1.954	-6.766	-4.505	2.262	-6.741	-4.477	2.264
MUSMQ-Prot-N-0	- 12.045	- 10.167	1.878	- 6.692	-4.477	2.214	-6.663	-4.436	2.227
SQ-Prot-U	- 9.184	- 6.699	2.485	-6.587	- 3.512	3.075	-6.566	- 3.482	3.084
MOSMO Prot-O	- 8.564	- 6.455	2.109	- 6.15/	- 3.442	2./16	- 6.138	- 3.412	2.726
INIO2INIQ-PT0E-O	- õ.445	-0.320	2.119	-0.115	-3.376	2.739	- 0.090	- 3.332	2.758

techniques and theoretical studies. According to experimental findings, it could be concluded that:

- 2. The thermodynamic parameters of activation and adsorption are calculated and discussed.
- 3. Quinoxalinone derivatives act as a mixed type inhibitors.
- 1. Quinoxalinone derivatives are good corrosion inhibitor for mild steel in 1.0 M HCl solution and its performance depends on its concentration and its molecular structures.
- 4. The high inhibition efficiency of the inhibitor was explained by adsorption of quinoxalinone derivatives molecules on mild steel surface.

- 5. The inhibition efficiency follows the order: MOSQ > MOSMQ > SQ.
- 6. EIS measurements also indicate that the inhibitor addition increases the charge transfer resistance and show that the inhibitive performance depends on molecules adsorption on metallic surface.
- Quantum chemical approach was adequately used to explain the correlation between the mild steel corrosion inhibition and molecular structure of compounds. It is found that the corrosion inhibition power of these products is closely related to its quantum chemical parameters.
- A good correlation is found between the energy of the LUMO and inhibition efficiency. The energy of the lowest unoccupied molecular orbital, *E_{LUMO}*, is indicative of the ability of the inhibitor molecule to accept electrons. So, the lower the value of *E_{LUMO}*, the greater the probability the molecule accepts electrons. Inhibition efficiency increases with decreasing LUMO energy.

References

- Y.G. Avdeev, Y.I. Kuznetsov, A.K. Buryak, Inhibition of steel corrosion by unsaturated aldehydes in solutions of mineral acids, Corros. Sci. 69 (2013) 50–60.
- [2] P.B. Raja, A.K. Qureshi, A.A. Rahim, H. Osman, K. Awang, Neolamarckia cadamba alkaloids as eco-friendly corrosion inhibitors for mild steel in 1 M HCl media, Corros. Sci. 69 (2013) 292–301.
- [3] B. Zerga, B. Hammouti, M. Ebn Touhami, R. Touir, M. Taleb, M. Sfaira, M. Bennajeh, I. Forssal, Comparative inhibition study of new synthesised pyridazine derivatives towards mild steel corrosion in hydrochloric acid. Part-II: Thermodynamic proprieties, Int. J. Electrochem. Sci. 7 (2012) 471–483.
- [4] K. Adardour, R. Touir, Y. Ramli, R.A. Belakhmima, M. Ebn Touhami, C. Kalonji Mubengayi, H. El Kafsaoui, E.M. Essassi, Comparative inhibition study of mild steel corrosion in hydrochloric acid by new class synthesized quinoxaline derivatives: part I, Res. Chem. Intermed. 39 (2013) 1843–1855.
- [5] J. Saranya, P. Sounthari, K. Parameswari, S. Chitra, Acenaphtho[1,2-b]quinoxaline and acenaphtho[1,2-b]pyrazine as corrosion inhibitors for mild steel in acid medium, Measurement 77 (2016) 175–186.
- [6] H. Zarrok, A. Zarrouk, R. Salghi, M. Ebn Touhami, H. Oudda, B. Hammouti, R. Touir, F. Bentiss, S.S. Al-Deyab, Corrosion inhibition of C38 steel in acidic medium using N-1 naphthylethylenediamine dihydrochloride monomethanolate, Int. J. Electrochem. Sci. 8 (2013) 6014–6032.
- [7] K. Adardour, R. Touir, M. Elbakri, Y. Ramli, M. Ebn Touhami, H. El Kafsaoui, C.K. Mubengayi, E.M. Essassi, Thermodynamic study of mild steel corrosion in hydrochloric acid by new class synthesized quinoxaline derivatives: part II, Res. Chem. Intermed. 39 (2013) 4175–4188.
- [8] R. Touir, R.A. Belakhmima, M. Ebn Touhami, L. Lakhrissi, M. El Fayed, B. Lakhrissi, E.M. Essassi, Comparative inhibition study of mild steel corrosion in hydrochloric acid by benzimidazole derivatives, J. Mater. Environ. Sci. 4 (6) (2013) 921–930.
- [9] J. Hmimou, A. Rochdi, R. Touir, M. Ebn Touhami, E.H. Rifi, A. El Hallaoui, A. Anouar, D. Chebab, Study of corrosion inhibition of mild steel in acidic medium by 2-propargyl-5-p-chlorophenyltetrazole : Part I, J. Mater. Environ. Sci. 3 (3) (2012) 543–550.
- [10] Y. Elkacimi, M. Achnin, Y. Aouine, M. Ebn Touhami, A. Alami, R. Touir, M. Sfaira, D. Chebabe, A. Elachqar, B. Hammouti, Inhibition of mild steel corrosion by some phenyltetrazole substituted compounds in hydrochloric acid, Port. Electrochim. Acta 30 (2012) 53–65.
- [11] T. Ghailane, R.A. Balkhmim, R. Ghailane, A. Souizi, R. Touir, M. Ebn Touhami, K. Marakchi, N. Komiha, Experimental and theoretical studies for mild steel corrosion inhibition in 1 M HCl by two new benzothiazine derivatives, Corros. Sci. 76 (2013) 317–324.
- [12] K. Adardour, R. Touir, M. El bakri, H. Larhzil, M. Ebn Touhami, Y. Ramli, A. Zarrouk, H. El Kafsaoui, E.M. Essassi, Thermodynamic properties and comparative studies of quinoxaline derivatives as a corrosion inhibitor for mild steel in 1 M H₂SO₄, Res. Chem. Intermed. 41 (2015) 1571–1589.
- [13] L.O. Olasunkanmi, M.M. Kabanda, E.E. Ebenso, Quinoxaline derivatives as corrosion inhibitors for mild steel in hydrochloric acid medium: electrochemical and quantum chemical studies, Phys. E. 76 (2016) 109–126.
- [14] A. Zarrouk, I. El Ouali, M. Bouachrine, B. Hammouti, Y. Ramli, E.M. Essassi, I. Warad, A. Aouniti, R. Salghi, Theoretical approach to the corrosion inhibition efficiency of some quinoxaline derivatives of steel in acid media using the DFT method, Res. Chem. Intermed. 39 (2013) 1125–1133.
- [15] F. Bentiss, M. Traisnel, L. Gengembre, M. Lagrenée, A new triazole derivative as inhibitor of the acid corrosion of mild steel: electrochemical studies, weight loss determination, SEM and XPS, Appl. Surf. Sci. 152 (1999) 237–249.
- [16] J. Saranya, P. Sounthari, A. Kiruthika, G. Saranya, S. Yuvarani, K. Parameswari, S. Chitra, Experimental and quantum chemical studies on the inhibition potential of some quinoxaline derivatives for mild steel in acid media, Orient. J. Chem. 30 (2014) 1719–1736.
- [17] B. Donnelly, T.C. Downie, R. Grzeskowiak, H.R. Hamburg, D. Short, The effect of electronic delocalization in organic groups R in substituted thiocarbamoyl R-CS-NH₂ and related compounds on inhibition efficiency, Corros. Sci. 18 (1978) 109–116.
- [18] A.B. Tadros, A.B. Adbennabey, Inhibition of the acid corrosion of steel by 4-amino-3hydrazino-5-thio-1,2,4-triazoles, J. Electroanal. Chem. 24 (1988) 433–439.

- [19] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, et al., Gaussian 03W, Gaussian Inc., Wallingford, CT, 2004.
- [20] C. Adamo, D. Jacquemin, The calculations of excited-state properties with timedependent density functional theory, Chem. Soc. Rev. 42 (2013) 845–856.
- [21] J.K. Landquist, G.J. Stacey, Quinoxaline N-oxides. Part II. Oxides of Py-substituted quinoxalines, J. Chem. Soc. (1953) 2822–2830.
- [22] W. Ried, S. Hinsching, Justus Liebigs Ann. Chem. 47 (1956) 600.
- [23] M.A. Philips, The formation of 2-substituted benziminazoles, J. Chem. Soc. 39 (1928) 2393–2399.
- [24] H. Lgaz, Y. ELaoufir, Y. Ramli, M. Larouj, H. Zarrok, R. Salghi, A. Zarrouk, A. Elmidaoui, A. Guenbour, E.L.M. Essassi, H. Oudda, Synergistic effect of potassium iodide with (E)-3-(4 methoxystyryl)quinoxalin- 2(1H)-one on the corrosion inhibition of carbon steel in 1.0 M HCl, Der Pharma Chem. 7 (2015) 36–45.
- [25] ASTM, Designation G1-03 "Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens", 2011.
- [26] H. Chermette, Chemical reactivity indexes in density functional theory, J. Comput. Chem. 20 (1999) 129–154.
- [27] R.G. Parr, P.K. Chattaraj, Principle of maximum hardness, J. Am. Chem. Soc. 113 (1991) 1854–1855.
- [28] V.R.P. Iczkowski, J.L. Margrave, Electronegativity, J. Am. Chem. Soc. 83 (1961) 3547–3551.
- [29] T. Koopmans, Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den Einzelnen Elektronen Eines Atoms, Physica 1 (1933) 104–113.
- [30] W. Yang, C. Lee, S.K. Ghosh, Molecular softness as the average of atomic softnesses: companion principle to the geometric mean principle for electronegativity equalization, J. Phys. Chem. 89 (1985) 5412–5414.
- [31] W. Yang, R.G. Parr, Hardness, softness, and the Fukui function in the electronic theory of metals and catalysis, Proc. Natl. Acad. Sci. 82 (1985) 6723–6726.
- [32] P.K. Chattaraj, U. Sarkar, D.R. Roy, Electrophilicity index, Chem. Rev. 106 (2006) 2065–2091.
- [33] R.G. Parr, L. Sventpaly, S. Liu, Electrophilicity index, J. Am. Chem. Soc. 121 (1999) 1922–1924.
- [34] C.M. Goulart, A. Esteves-Souza, C.A. Martinez-Huitle, C.J.F. Rodrigues, M.A.M. Maciel, A. Echevarria, Experimental and theoretical evaluation of semicarbazones and thiosemicarbazones as organic corrosion inhibitors, Corros. Sci. 67 (2013) 281–291.
- [35] Y. Abbouda, A. Abourriche, T. Saffaj, M. Berrada, M. Charrouf, A. Bennamara, N. Al Himidi, H. Hannache, 2,3-Quinoxalinedione as a novel corrosion inhibitor for mild steel in 1 M HCl, Mater. Chem. Phys. 105 (2007) 1–5.
- [36] K.F. Khaled, The inhibition of benzimidazole derivatives on corrosion of iron in 1 M HCl solutions, Electrochim. Acta 48 (2003) 2493–2503.
- [37] H. Gerengi, K. Darowicki, G. Bereket, P. Slepski, Evaluation of corrosion inhibition of brass-118 in artificial seawater by benzotriazole using dynamic EIS, Corros. Sci. 51 (2009) 2573–2579.
- [38] A. Popova, M. Christov, A. Vasilev, Inhibitive properties of quaternary ammonium bromides of N-containing heterocycles on acid mild steel corrosion. Part II: EIS results, Corros. Sci. 49 (2007) 3290–3302.
- [39] H. Ashassi-Sorkhabi, D. Seifzadeh, M. Hosseini, EN, EIS and polarization studies to evaluate the inhibition effect of 3H-phenothiazin-3-one, 7-dimethylamin on mild steel corrosion in 1M HCl solution, Corros. Sci. 50 (2008) 3363–3370.
- [40] A. Popova, M. Christov, A. Vasilev, Mono- and dicationic benzothiazolic quaternary ammonium bromides as mild steel corrosion inhibitors. Part II: Electrochemical impedance and polarisation resistance results, Corros. Sci. 53 (2011) 1770–1777.
- [41] K.F. Khaled, M.M. Al-Qahtani, Mater. Chem. Phys. 113 (2009) 150–158.
- [42] S.S. El-Rehim, M.A.M. Ibrahim, K.F. Khaled, 4-Aminoantipyrine as an inhibitor of mild steel corrosion in HCl solution, J. Appl. Electrochem. 29 (1999) 593–599.
- [43] L. Fragoza-Mar, O. Olivares-Xometl, M.A. Domínguez-Aguilar, E.A. Flores, P. Arellanes-Lozada, F. Jiménez-Cruz, Corrosion inhibitor activity of 1,3-diketone malonates for mild steel in aqueous hydrochloric acid solution, Corros. Sci. 61 (2012) 171–184.
- [44] M. Bouklah, B. Hammouti, M. Lagrenee, F. Bentiss, Thermodynamic properties of 2,5bis(4-methoxyphenyl)-1,3,4-oxadiazole as a corrosion inhibitor for mild steel in normal sulfuric acid medium, Corros. Sci. 48 (2006) 2831–2842.
- [45] A. Popova, E. Sokolova, S. Raicheva, M. Christov, AC and DC study of the temperature effect on mild steel corrosion in acid media in the presence of benzimidazole derivatives, Corros. Sci. 45 (2003) 33–58.
- [46] M. Elayyachy, M. Elkodadi, A. Aouniti, A. Ramdani, B. Hammouti, F. Malek, A. Elidrissi, New bipyrazole derivatives as corrosion inhibitors for steel in hydrochloric acid solutions, Mater. Chem. Phys. 93 (2005) 281–285.
- [47] T. Szauer, A. Brand, Adsorption of oleates of various amines on iron in acidic solution, Electrochim. Acta 26 (1981) 1253–1256.
- [48] E.A. Noor, Temperature effects on the corrosion inhibition of mild steel in acidic solutions by aqueous extract of fenugreek Leaves, Int. J. Electrochem. Sci. 2 (2007) 996–1017.
- [49] A.K. Singh, M.A. Quraishi, Investigation of the effect of disulfiram on corrosion of mild steel in hydrochloric acid solution, Corros. Sci. 53 (2011) 1288–1297.
- [50] A.K. Singh, S.K. Shukla, M. Singh, M.A. Quraishi, Inhibitive effect of ceftazidime on corrosion of mild steel in hydrochloric acid solution, Mater. Chem. Phys. 129 (2011) 68–76.
- [51] M. Lebrini, F. Bentiss, H. Vezin, M. Lagrenee, The inhibition of mild steel corrosion in acidic solutions by 2,5-bis(4-pyridyl)-1,3,4- thiadiazole: structure–activity correlation, Corros. Sci. 48 (2006) 1279–1291.
- [52] F. Bentiss, M. Lebrini, M. Lagrenee, Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in mild steel/2,5-bis(n-thienyl)-1,3,4thiadiazoles/hydrochloric acid system, Corros. Sci. 47 (2005) 2915–2931.
- [53] A.M. Badiea, K.N. Mohana, Effect of temperature and fluid velocity on corrosion mechanism of low carbon steel in presence of 2-hydrazino- 4,7-

dimethylbenzothiazole in industrial water medium, Corros. Sci. 51 (2009) 2231–2241.

- [54] Z. Szklarska-Smialowska, J. Mankowski, Crevice corrosion of stainless steels in sodium chloride solution, Corros. Sci. 18 (1978) 953–960.
- [55] A. Yurt, S. Ulutas, H. Dal, Electrochemical and theoretical investigation on the corrosion of aluminium in acidic solution containing some Schiff bases, Appl. Surf. Sci. 253 (2006) 919–925.
- [56] F. Hongbo, Synthesis and Application of New Type Inhibitors, Chemical Industry Press, Beijing, 2002 166.
- [57] H.-L. Wang, H.-B. Fan, J.-S. Zheng, Corrosion inhibition of mild steel in hydrochloric acid solution by a mercapto-triazole compound, Mater. Chem. Phys. 77 (2003) 655–661.
- [58] W. Durnie, R.D. Marco, A. Jefferson, B. Kinsella, Development of a structure-activity relationship for oil field corrosion inhibitors, J. Electrochem. Soc. 146 (1999) 1751–1756.
- [59] M.A. Amin, M.A. Ahmed, H.A. Arida, F. Kandemirli, M. Saracoglu, T. Arslan, Monitoring corrosion and corrosion control of iron in HCl by non-ionic surfactants of the TRITON-X series-Part III. Immersion time effects and theoretical studies, Corros. Sci. 53 (2011) 1895–1909.
- [60] S. Zor, M. Saracoglu, F. Kandemirli, T. Arslan, Inhibition effects of amides on the corrosion of copper in 1.0 M HCI: theoretical and experimental studies, corrosion, J. Sci. Eng. 67 (2011) 125003-1–125003-11.
- [61] E.E. Ebenso, M.M. Kabanda, T. Arslan, M. Saracoglu, F. Kandemirli, L.C. Murulana, A.K. Singh, S.K. Shukla, B. Hammouti, K.F. Khaled, M.A. Quraishi, I.B. Obot, N.O. Eddy, Quantum chemical investigations on quinoline derivatives as effective corrosion inhibitors for mild steel in acidic medium, Int. J. Electrochem. Sci. 7 (2012) 5643–5676.
- [62] F. Kandemirli, M. Saracoglu, M.A. Amin, M.A. Basaran, C.D. Vurdu, The quantum chemical calculations of serine, therionine and glutamine, Int. J. Electrochem. Sci. 9 (2014) 3819–3827.

- [63] I.B. Obot, N.O. Obi-Egbedi, Theoretical study of benzimidazole and its derivatives and their potential activity as corrosion inhibitors, Corros. Sci. 52 (2010) 657–660.
- [64] I.B. Obot, D.D. Macdonald, Z.M. Gasem, Density functional theory (DFT) as a powerful tool for designing new organic corrosion inhibitors. Part 1: An overview, Corros. Sci. 99 (2015) 1–30.
- [65] A. Özalp, Z. Kökbudak, M. Saracoglu, F. Kandemirli, I.Ö. Ilhan, C.D. Vurdu, Synthesis and theoretical study of the novel 2-oxopyrimidin-1(2H)-ylamides derivative, Chem. Sci. Rev. Lett. 4 (2015) 719–728.
- [66] S. Kaya, B. Tuzun, C. Kaya, I.B. Obot, Determination of corrosion inhibition effects of amino acids: quantum chemical and molecular dynamic simulation study, J. Taiwan Ins. Chem. Eng. (2015), http://dx.doi.org/10.1016/j.jtice.2015.06.009.
- [67] S. Kaya, C. Kaya, A new equation for calculation of chemical hardness of groups and molecules, Mol. Phys. 113 (2015) 1311–1319.
- [68] S. Kaya, C. Kaya, A new method for calculation of molecular hardness: a theoretical study, Comput. Theor. Chem. 1060 (2015) 66–70.
- [69] R.G. Pearson, Recent advances in the concept of hard and soft acids and bases, J. Chem. Educ. 64 (1987) 561–567.
- [70] S. Kaya, C. Kaya, A new equation based on ionization energies and electron affinities of atoms for calculating of group electronegativity, Comput. Theor. Chem. 1052 (2015) 42–46.
- [71] I.B. Obot, Z.M. Gasem, Theoretical evaluation of corrosion inhibition performance of some pyrazine derivatives, Corros. Sci. 83 (2014) 359–366.
- [72] N.O. Obi-Egbedi, I.B. Obot, Inhibitive properties, thermodynamic and quantum chemical studies of alloxazine on mild steel corrosion in H2SO4, Corros. Sci. 53 (2011) 263–275.
- [73] C. Kaya, Inorganic Chemisry 1 and 2, Palme Publishing, Ankara, 2011.
- [74] G. Gece, S. Bilgic, Molecular-level understanding of the inhibition efficiency of some inhibitors of zinc corrosion by quantum chemical approach, Ind. Eng. Chem. Res. 51 (2012) 14115–14120.