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The adsorption and corrosion inhibition of 8-hydroxy-7-quinolinecarboxaldehyde derivatives on C-steel surface in hydrochloric acid

A.M. Eldesoky^{1,2}, S.G. Nozha^{3,*}¹ Engineering Chemistry Department, High Institute of Engineering & Technology, New Damietta, Egypt² Al-Qunfudah Center for Scientific Research (QCSR), Al-Qunfudah University College, Umm Al-Qura University, Saudi Arabia³ Ministry of Health, Domyat Laboratory, Damietta, Egypt

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ABSTRACT

The protection influence of 8-hydroxy-7-quinolinecarboxaldehyde derivatives against C-steel corrosion was studied in 2 mol·L⁻¹ HCl solutions at 30 °C. Measurements were conducted under various experimental conditions using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques. These studies have shown that 8-hydroxy-7-quinolinecarboxaldehyde derivatives are very good “green”, mixed-type inhibitors. Corrosion rates obtained from both EFM and EIS methods are comparable with those recorded using Tafel extrapolation method, confirming validation of corrosion rates measured by the latter. The inhibitive action of these 8-hydroxy-7-quinolinecarboxaldehyde derivatives was discussed in terms of blocking the electrode surface by adsorption of the molecules through the active centers contained in their structures following Langmuir adsorption isotherm. Quantum chemical method was also employed to explore the relationship between the inhibitor molecular properties and its protection efficiency.

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1. Introduction

Carbon steel has been extensively used under different conditions in petroleum industries [1]. Aqueous solutions of acids are among the most corrosive media and are widely used in industries for pickling, acid cleaning of boilers and oil well [2–6]. The main problem concerning C-steel applications is its relatively low corrosion resistance in acidic solution. Several methods were used currently to reduce corrosion of C-steel. One of such methods is the use of organic inhibitors [7–11]. The effect of aniline compounds, on the corrosion of mild steel in HCl has been studied [12]. Effective inhibitors are heterocyclic compounds that have π bonds, heteroatoms such as sulfur, oxygen or nitrogen and the sites of these elements are considered as chemisorption center [13]. These elements possess higher electron density and are called as electroactive groups. The electron density on these centers is the direct measure of IE of the inhibitor [14]. These molecules depend mainly on certain physical properties of the inhibitor molecules such as functional groups, steric factors, electron density at the donor atom and electronic structure of the molecules [15,16]. Regarding the adsorption of the inhibitor on the metal surface, two types of interactions are responsible. One is physical adsorption which involves

electrostatic force between ionic charges or dipoles of the adsorbed species and electric charge at metal/solution interface. Other is chemical adsorption, which involves charge sharing or charge transfer from inhibitor molecules to the metal surface to form coordinated types of bonds [17]. The selection of appropriate inhibitors mainly depends on the type of acid, its concentration, and temperature. The influence of such quinolines and their derivatives (N-heterocyclic compounds) on the corrosion of mild steel in acidic solution has been mentioned by many authors [18–22]. Although some Schiff base quinoline derivatives have been reported as corrosion inhibitors for steel in acidic medium [20–22], no work to the best of our knowledge has been documented on the corrosion inhibition potentials of azo quinoline derivatives.

The objective of the present investigation is to study the corrosion inhibition of C-steel in 2 mol·L⁻¹ HCl using 8-hydroxy-7-quinolinecarboxaldehyde derivatives and to propose a suitable mechanism for the inhibition process. It was also the purpose of the present work to discuss the relationship between quantum chemical calculations and experimental protection efficiencies of the tested 8-hydroxy-7-quinolinecarboxaldehyde derivatives by determining various quantum chemical parameters. These parameters include the highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO} .

* Corresponding author.

E-mail address: samar.nozha@gmail.com (S.G. Nozha).

2. Experimental

2.1. Composition of material samples

Table 1
Chemical composition of the C-steel in weight %

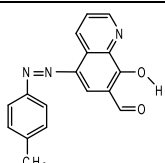
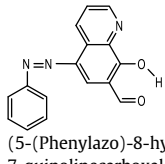
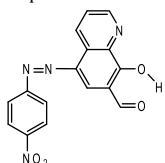
Element	C	Mn	P	Si	Fe
Weight/%	0.200	0.350	0.024	0.003	rest

2.2. Chemicals and solutions

Hydrochloric acid (37%), ethyl alcohol was purchased from Al-gomhoria Company. Bidistilled water was used throughout all the experiments.

The organic inhibitors used in this study were some 8-hydroxy-7-quinolinecarboxaldehyde derivatives, listed in Table 2.

Table 2
Chemical structure, names, molecular weights and molecular formula of inhibitors

Compound	Structure	Empirical formula	Molecular weight
HL ₁	 (5-(4'-Methylphenylazo)-8-hydroxy-7-quinolinecarboxaldehyde)	C ₁₇ H ₁₃ N ₃ O ₂	291.31
HL ₂	 (5-(Phenylazo)-8-hydroxy-7-quinolinecarboxaldehyde)	C ₁₆ H ₁₁ N ₃ O ₂	277.28
HL ₃	 (5-(4'-Nitrophenylazo)-8-hydroxy-7-quinolinecarboxaldehyde)	C ₁₆ H ₁₀ N ₄ O ₄	322.28

8-Hydroxy-7-quinolinecarboxaldehyde was prepared according to El-Sonbati and El-Bindary [23]. 8-Hydroxy-7-quinolinecarboxaldehyde (HL_n) was prepared according to El-sonbati *et al.* [24,25]. As following, azo dye ligands (HL_n) were prepared from aniline or its *p*-substituted derivatives (10 mmol) were dissolved in hydrochloric acid (20 mmol/25 ml distilled H₂O). The hydrochloric compound was diazotized below 0–5 °C with a solution of sodium nitrite (0.8 g, 10 mmol, 30 ml distilled H₂O). The diazonium chloride was coupled with an alkaline solution of oxine (1.7 g, 10 mmol) in 20 ml of pyridine. The crude dye was collected by filtration and was crystallized from DMF, then dried in a vacuum desiccator over P₂O₅.

2.3. Methods

2.3.1. Mass loss measurements

Rectangular specimens of C-steel with dimensions 2.1 cm × 2.0 cm × 0.2 cm were abraded with different grades of emery paper, degreased with acetone, rinsed with bidistilled water and dried between filter

papers. After weighting accurately, the specimens were immersed in 100 ml of 2 mol·L⁻¹ HCl with and without different concentrations of inhibitors at 30 °C. After different immersion periods, the C-steel samples were taken out, washed with bidistilled water, dried and weighted again. The mass loss values are used to calculate the corrosion rate (*R*) in mm·a⁻¹ by Eq. (1):

$$R = (\text{mass loss in gram} \times 8.75 \times 10^4) / DAT \quad (1)$$

where *D* is the Fe density in g·cm⁻³, *A* is the exposed area in cm²; *T* is exposure time in hour. The inhibition efficiency (IE) and the degree of surface coverage (*θ*) were calculated from Eq. (2):

$$IE = \theta \times 100 = [(R^* - R) / R^*] \times 100\% \quad (2)$$

where *R*^{*} and *R* are the corrosion rates of C-steel in the absence and in the presence of inhibitor, respectively.

2.3.2. Electrochemical measurements

Electrochemical measurements were conducted in a conventional three electrodes thermostated cell assembly using a Gamry potentiostat/galvanostat/ZRA (model PCI300/4). A platinum foil and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The C-steel electrodes were 1 cm × 1 cm and were welded from one side to a copper wire used for electrical connection. The electrodes were abraded, degreased and rinsed as described in weight loss measurements. All experiments were carried out at temperature (30 ± 1) °C. The potentiodynamic curves were recorded from -500 to 500 mV at a scan rate 1 mV·s⁻¹ after the steady state is reached (30 min) and the open circuit potential (OCP) was noted. The IE and degree of surface coverage were calculated from Eq. (3):

$$IE = \theta \times 100 = \left[1 - \left(i_{\text{corr}}^0 / i_{\text{corr}} \right) \right] \times 100\% \quad (3)$$

where *i*_{corr}⁰ and *i*_{corr} are the corrosion current densities of uninhibited and inhibited solution, respectively.

Electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) experiments were carried out using the same instrument as before with a Gamry framework system based on ESA400. Gamry applications include software EIS300 for EIS measurements and EFM140 for EFM measurements; computer was used for collecting data. Echem Analyst 5.5 Software was used for plotting, graphing and fitting data. EIS measurements were carried out in a frequency range of 100 kHz to 10 mHz with amplitude of 5 mV peak-to-peak using ac signals at respective corrosion potential. EFM carried out using two frequencies 2 and 5 Hz. The base frequency was 1 Hz. In this study, we use a perturbation signal with amplitude of 10 mV for both perturbation frequencies of 2 and 5 Hz.

2.3.3. Theoretical study

The molecular structures of the investigated compounds were optimized initially with PM3 semiempirical method so as to speed up the calculations. The resulting optimized structures were fully re-optimized using an initio Hartree–Fock (HF) with 6-31G basis set. The molecules were built with the Gauss View 3.09 and optimized using Gaussian 03 W program [25].

3. Results and Discussion

3.1. Mass loss measurements

Fig. 1 shows the mass loss–time curves for the corrosion of C-steel in 2 mol·L⁻¹ HCl in the absence and presence of different concentrations of compound (HL₁). Similar curves for other compounds were obtained (not shown). The data of Table 3 show that, the inhibition efficiency increases with increase in inhibitor concentration from 1 × 10⁻⁶ to

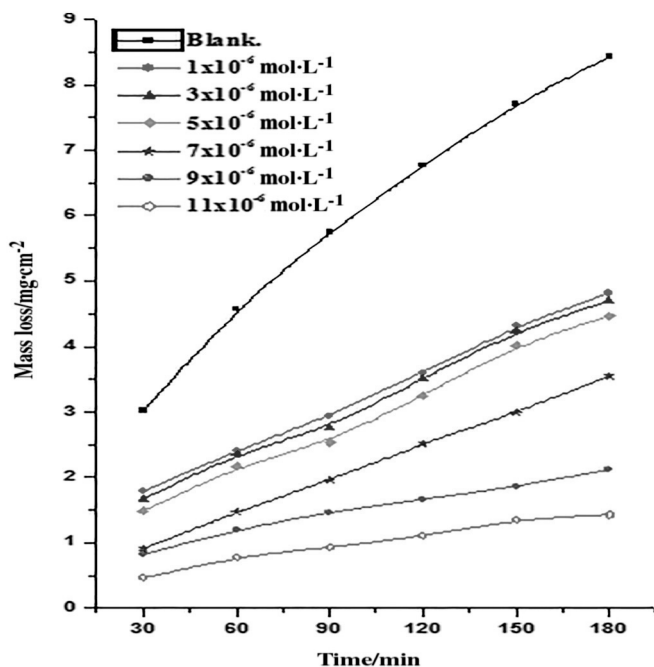


Fig. 1. Weight loss-time curves for C-steel dissolution in 2 mol·L⁻¹ HCl in the absence and presence of different concentrations of compound (HL₁) at (30 ± 1) °C.

Table 3

Variation of inhibition efficiency (IE) of different compounds with their molar concentrations from mass loss measurements at 120 min immersion in 2 mol·L⁻¹ HCl at (30 ± 1) °C

Conc./mol·L ⁻¹	Inhibition efficiency (IE)		
	HL ₁	HL ₂	HL ₃
1 × 10 ⁻⁶	46.7	32	24.6
3 × 10 ⁻⁶	55.1	39.4	30.5
5 × 10 ⁻⁶	59.1	46.7	38.4
7 × 10 ⁻⁶	68.1	57.6	44.7
9 × 10 ⁻⁶	82.9	70.2	60.7
11 × 10 ⁻⁶	87.6	78.9	72.6

11 × 10⁻⁶ mol·L⁻¹. The maximum inhibition efficiency was achieved at 11 × 10⁻⁶ mol·L⁻¹; therefore IE tends to decrease in the following order:

Compound (HL₁) > compound (HL₂) > compound (HL₃).

3.1.1. Adsorption isotherm

The adsorption isotherms are considered to describe the interactions of the inhibitor molecule with the active sites on the metal surface [26]. Attempts were made to fit θ values to various isotherms including Frumkin, Langmuir, Temkin, and Freundlich. The results were best fitted by far by the Langmuir adsorption isotherm which has the following equation [27,28]:

$$C/\theta = 1/K_{\text{ads}} + C \quad (4)$$

where C is the concentration of inhibitor; K_{ads} is the adsorptive equilibrium constant; and θ is the surface coverage of 8-hydroxy-7-quinolinecarboxaldehyde derivatives on carbon steel, which can be calculated by the ratio of IE/100 for different inhibitors concentrations [29]. Fig. 2 show the straight lines of C/θ vs. C at (30 °C). The linear correlation coefficients (0.926), (0.85851) and (0.7017) at 30 °C

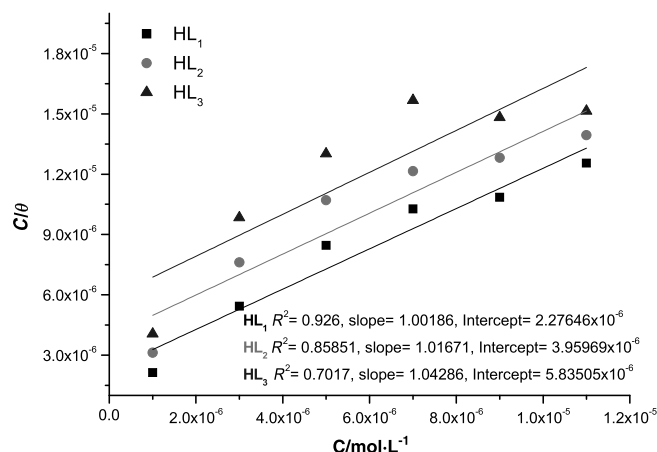


Fig. 2. Curve fitting of corrosion data for C-steel surface in hydrochloric acid in presence of different concentrations of organic additives to the Langmuir adsorption isotherm at (30 ± 1) °C.

are almost equal to 1 and the slopes (1.0018), (1.016) and (1.042) at 30 °C are close to 1, which confirms the assumption that the adsorption of 8-hydroxy-7-quinolinecarboxaldehyde derivative compounds on the carbon steel surface obeys Langmuir adsorption isotherm. The adsorptive equilibrium constants at T (30 °C) namely K are (4.39×10^5), (2.53×10^5) and (1.71×10^5) L·mol⁻¹, respectively.

The standard adsorption free energy ($\Delta G_{\text{ads}}^\ominus$) can be obtained according to the following equation [30,31].

$$K_{\text{ads}} = 1/55.5 \exp \left(-\Delta G_{\text{ads}}^\ominus / RT \right) \quad (5)$$

The negative values of $\Delta G_{\text{ads}}^\ominus$ (Table 4) suggest that the adsorption of 8-hydroxy-7-quinolinecarboxaldehyde derivatives on the carbon steel surface is spontaneous. Generally, the values of $\Delta G_{\text{ads}}^\ominus$ around or less than -20 kJ·mol⁻¹ are associated with the electrostatic interaction between charged molecules and the charged metal surface (physisorption); while those around or higher than -40 kJ·mol⁻¹ mean charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of metal bond (chemisorption) [32]. The values of $\Delta G_{\text{ads}}^\ominus$ obtained were approximately equal to (42.85–40.48) kJ·mol⁻¹, indicating that the adsorption mechanism of these investigated 8-hydroxy-7-quinolinecarboxaldehyde derivatives on C-steel in 2 mol·L⁻¹ HCl solution involves both electrostatic adsorption and chemisorptions [33,34]. The thermodynamic parameters point towards both physisorption (minor contributor) and chemisorptions (major contributor) of the inhibitors onto the metal surface. The K_{ads} follows the same trend in the sense that large values of K_{ads} imply better more efficient adsorption and hence better inhibition efficiency.

Table 4

Binding constant (K) and free energy of adsorption ($\Delta G_{\text{ads}}^\ominus$) of inhibitors with their molar concentrations at (30 ± 1) °C from mass loss measurements at 120 min immersion in 2 mol·L⁻¹ HCl

Compound	$K \times 10^5$	$-\Delta G_{\text{ads}}^\ominus / \text{kJ} \cdot \text{mol}^{-1}$
HL ₁	4.39	42.85
HL ₂	2.53	41.46
HL ₃	1.71	40.48

3.1.2. Effect of temperature

The activation energies (E_a^*) for the corrosion of C-steel in the absence and presence of different concentrations of 8-hydroxy-7-

quinolinecarboxaldehyde derivatives were calculated using Arrhenius-type Eq. [35]:

$$\log k = \log A - E_a^*/2.303RT \quad (6)$$

where A is the pre-exponential factor, k is the rate constant, E_a^* is the apparent activation energy of the corrosion process, R is the universal gas constant and T is the absolute temperature. Arrhenius plots of $\log k$ vs. $1/T$ for C-steel in $2 \text{ mol} \cdot \text{L}^{-1}$ HCl in the absence and presence of different concentrations of inhibitor (HL_1) are shown graphically in Fig. 3. The variation of $\log k$ vs. $1/T$ is a linear one and the values of E_a^* were calculated from the slope of these lines and given in Table 5. The increase in E_a^* with the addition of concentration of inhibitors (HL_1 – HL_3) indicating that the energy barrier for the corrosion reaction increases. It is also indicated that the whole process is controlled by surface reaction, since the activation energy of the corrosion process is larger than $20 \text{ kJ} \cdot \text{mol}^{-1}$.

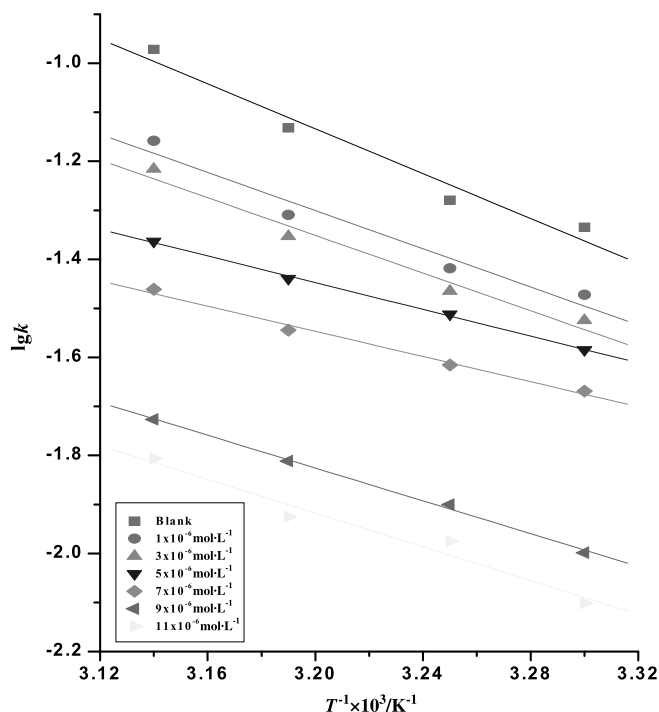


Fig. 3. Arrhenius plots ($\lg k$ vs. $1/T$) for corrosion of C-steel surface in hydrochloric acid in the absence and presence of different concentrations of compound (HL_1).

Enthalpy and entropy of activation (ΔH^* , ΔS^*) for the corrosion of C-steel in $2 \text{ mol} \cdot \text{L}^{-1}$ HCl were obtained by applying the transition state Eq. (7):

$$k = (RT/Nh) \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \quad (7)$$

where h is the Planck's constant, N is the Avogadro's number. A plot of $\log k/T$ vs. $1/T$ also gave straight lines as shown in Fig. 4 for C-steel dissolution in $2 \text{ mol} \cdot \text{L}^{-1}$ HCl in the absence and presence of different concentrations of inhibitor (HL_1). The slopes of these lines equal $-\Delta H^*/2.303R$ and the intercept equals $\log RT/Nh + (\Delta S^*/2.303R)$ from which the value of ΔH^* and ΔS^* was calculated and tabulated in Table 5. From these results, it is clear that the presence of the tested compounds increased the activation energy values and consequently decreased the corrosion rate of the C-steel. These results indicate that these tested compounds acted as inhibitors through increasing activation energy of C-steel dissolution by making a barrier

Table 5

Thermodynamic activation parameters for the dissolution of C-steel surface in hydrochloric acid in the absence and presence of different concentrations of investigated compounds

Compound	Conc./ $\text{mol} \cdot \text{L}^{-1}$	$E_a^*/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta H^*/\text{kJ} \cdot \text{mol}^{-1}$	$-\Delta S^*/\text{J} \cdot \text{mol}^{-1}$
Blank	–	25.42	22.84	299.83
HL_1	1×10^{-6}	28.68	26.10	194.62
	3×10^{-6}	29.13	26.55	190.63
	5×10^{-6}	30.30	27.02	180.72
	7×10^{-6}	30.91	28.33	172.04
	9×10^{-6}	34.65	32.06	170.49
HL_2	11×10^{-6}	34.93	31.95	169.73
	1×10^{-6}	28.49	25.91	195.25
	3×10^{-6}	29.09	26.41	191.83
	5×10^{-6}	29.34	26.76	182.34
	7×10^{-6}	30.39	27.81	173.99
HL_3	9×10^{-6}	32.88	30.30	172.15
	11×10^{-6}	34.65	31.07	170.79
	1×10^{-6}	18.12	15.94	219.81
	3×10^{-6}	20.12	17.54	259.02
	5×10^{-6}	24.90	18.32	261.18
	7×10^{-6}	25.99	23.41	269.52
	9×10^{-6}	27.21	25.63	271.47
	11×10^{-6}	28.73	26.15	288.51

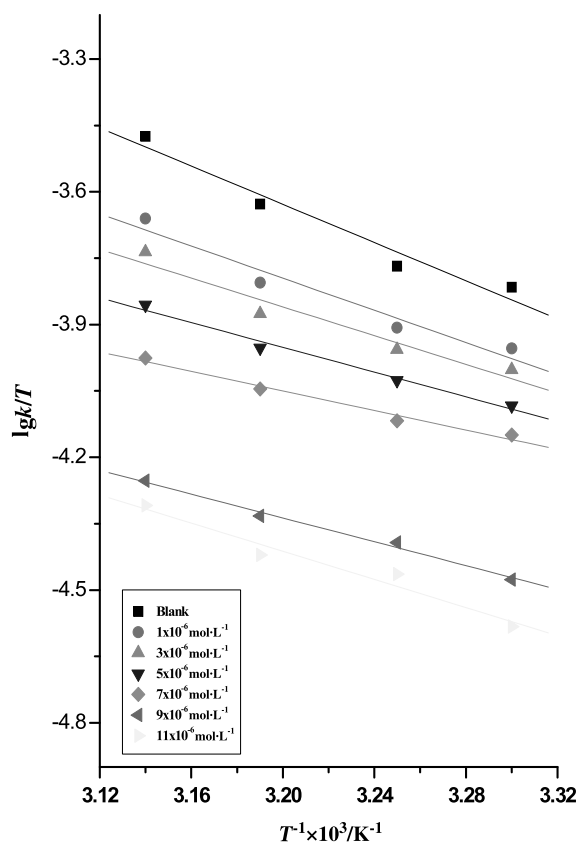


Fig. 4. Plots of ($\lg k/T$) vs. $1/T$ for corrosion of C-steel surface in hydrochloric acid in the absence and presence of different concentrations of compound (HL_1).

to mass and charge transfer by their adsorption on C-steel surface. Positive sign of the enthalpies reflects the endothermic nature of the C-steel dissolution process.

All values of E_a^* are larger than the analogous values of ΔH^* indicating that the corrosion process must involved a gaseous reaction, simply the hydrogen evolution reaction, associated with a decrease in the total reaction volume [36]. The values of ΔS^* in the absence and presence of the tested compounds are large and negative; this indicates that the activated complex in the rate-determining step represents an

association rather than dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [37,38].

3.2. Potentiodynamic polarization studies

The cathodic and anodic polarization curves for C-steel in $2 \text{ mol} \cdot \text{L}^{-1}$ HCl solution in absence and presence of various concentrations of the inhibitor (HL_1) at $(30 \pm 1)^\circ\text{C}$ are shown in Fig. 5. Similar curves were obtained for other inhibitors (not shown). The various electrochemical parameters calculated from Tafel plots are given in Table 6. The lower corrosion current density (i_{corr}) values in the presence of the inhibitors without causing significant changes in corrosion potential (E_{corr}) suggest that the investigated compounds are mixed type inhibitors and are adsorbed on the surface thereby blocking the corrosion reaction.

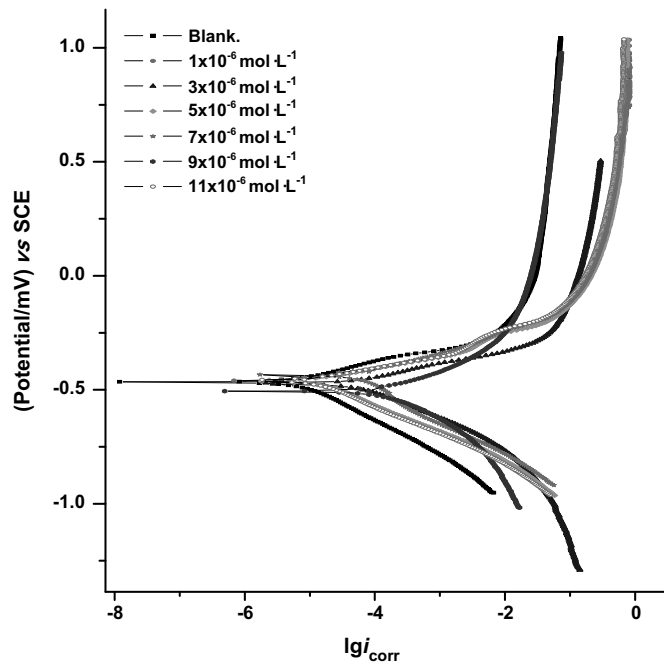


Fig. 5. Potentiodynamic polarization curves for the corrosion of C-steel surface in hydrochloric acid in the absence and presence of various concentrations of compound (HL_1) at $(30 \pm 1)^\circ\text{C}$.

Table 6

The effect of concentration of the investigated compounds on the free corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (β_a and β_c), inhibition efficiency (IE) and degree of surface coverage for the corrosion of C-steel surface in hydrochloric acid at $(30 \pm 1)^\circ\text{C}$

Compound	Conc./mol · L ⁻¹	$-E_{\text{corr}}$ (vs SCE)/mV	$i_{\text{corr}} \times 10^{-6}/\mu\text{A} \cdot \text{cm}^{-2}$	$\beta_a \times 10^{-3}/\text{mV} \cdot \text{dec}^{-1}$	$\beta_c \times 10^{-3}/\text{mV} \cdot \text{dec}^{-1}$	θ	IE/%
HL_1	Blank	466	9.42	92.7	181.0	–	–
	1×10^{-6}	501	1.40	90.9	133.0	0.851	85.1
	3×10^{-6}	461	1.16	92.0	179.6	0.877	87.7
	5×10^{-6}	498	1.11	86.5	124.6	0.882	88.2
	7×10^{-6}	502	1.09	86.5	120.1	0.884	88.4
	9×10^{-6}	480	1.05	106.4	155.4	0.888	88.8
	11×10^{-6}	497	1.04	89.1	119.7	0.889	88.9
HL_2	1×10^{-6}	460	1.76	70.2	149.2	0.813	81.3
	3×10^{-6}	472	1.63	36.7	59.0	0.827	82.7
	5×10^{-6}	461	1.62	66.2	136.4	0.828	82.8
	7×10^{-6}	434	1.58	38.5	95.9	0.832	83.2
	9×10^{-6}	506	1.54	100.6	150.6	0.836	83.6
	11×10^{-6}	460	1.41	62.7	138.6	0.850	85.0
HL_3	1×10^{-6}	466	9.07	88.0	204.8	0.0372	3.7
	3×10^{-6}	466	9.00	93.4	222.1	0.036	3.6
	5×10^{-6}	502	3.48	42.5	66.7	0.631	63.1
	7×10^{-6}	466	2.67	48.0	87.3	0.716	71.6
	9×10^{-6}	474	2.09	94.0	141.6	0.778	77.8
	11×10^{-6}	455	1.84	65.2	137.7	0.805	80.5

The results also show that the slopes of the anodic and the cathodic Tafel slopes (β_a and β_c) were slightly changed on increasing the concentration of the tested compounds. This indicates that there is no change in the mechanism of inhibition in the presence and absence of

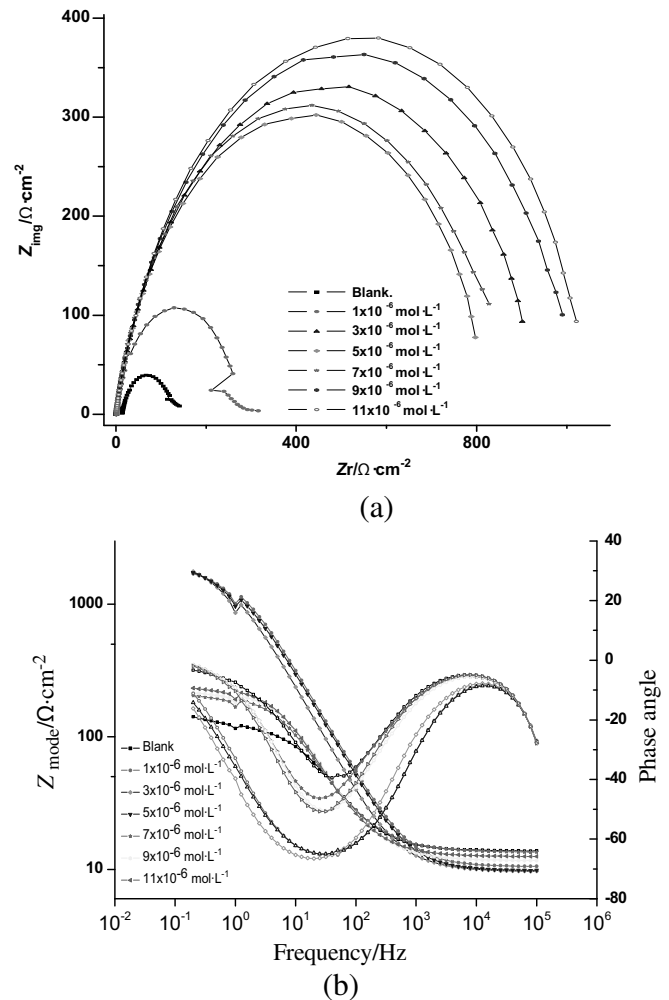


Fig. 6. EIS Nyquist plots (a) and Bode plots (b) for C-steel surface in hydrochloric acid in the absence and presence of different concentrations of compound (HL_1) at $(30 \pm 1)^\circ\text{C}$.

inhibitors. The values of β_c are slightly higher than the values of β_a suggesting a cathodic action of the inhibitor. The higher values of Tafel slope can be attributed to surface kinetic process rather the diffusion-controlled process [39,40].

3.3. Electrochemical impedance spectroscopy

The EIS provides important mechanistic and kinetic information for an electrochemical system under investigation. Fig. 6 shows the Nyquist (a) and Bode (b) plots obtained at open-circuit potential both in the absence and presence of increasing concentrations of investigated compound at $(30 \pm 1)^\circ\text{C}$. Nyquist impedance plots exhibits a single semi-circle shifted along the real impedance (Z_r). The Nyquist plots of compound (HL_1) do not yield perfect semicircles as expected from the theory of EIS, the impedance loops measured are depressed semi-circles with their centers below the real axis, where the kind of phenomenon is known as the “dispersing effect” as a result of frequency dispersion [41] and mass transport resistant [15] as well as electrode surface heterogeneity resulting from surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitors, formation of porous layers [42–44], etc. so one constant phase element (CPE) is substituted for the capacitive element, to explain the depression of the capacitance semi-circle, to give a more accurate fit. Impedance data are analyzed using the circuit in Fig. 7; in which R_s represents the electrolyte resistance, R_{ct} represents the charge-transfer resistance and

the constant phase element (CPE). According to Hsu and Mansfeld [45] the correction of capacity to its real values is calculated from Eq. (8):

$$C_{dl} = Y_o(\omega_{\max})^{n-1} \quad (8)$$

where Y_o is the CPE coefficient, $\omega_{\max}$ is the frequency at which the imaginary part of impedance ($-Z_i$) has a maximum and n is the CPE exponent (phase shift).

The data obtained from fitted spectra are listed in Table 7. The IE was calculated from Eq. (9):

$$IE = \left(1 - \frac{R_{ct}^*}{R_{ct}}\right) \times 100\% \quad (9)$$

where R_{ct} and R_{ct}^* are the charge-transfer resistances with and without the inhibitors, respectively.

Data in Table 7 show that the R_s values are very small compared to the R_{ct} values. Also, the R_{ct} values increase and the calculated C_{dl} values decrease by increasing the inhibitor concentrations, which causes an increase of θ and Y_i . The high R_{ct} values are generally associated with slower corroding system [40,46]. The decrease in the C_{dl} suggests that inhibitors function by adsorption at the metal/solution interface.

The inhibition efficiencies, calculated from EIS results, show the same trend as those obtained from polarization measurements. The difference of inhibition efficiency from two methods may be attributed

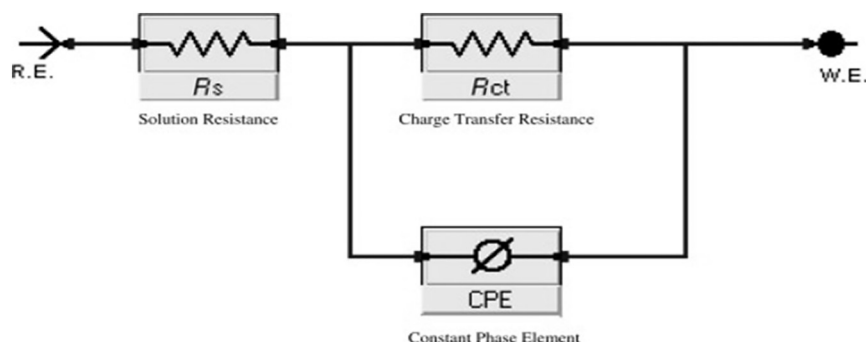


Fig. 7. Equivalent circuit model used to fit experimental EIS.

Table 7

Electrochemical kinetic parameters obtained from EIS technique for C-steel surface in hydrochloric acid in the absence and presence of different concentrations of investigated compounds at $(30 \pm 1)^\circ\text{C}$

Compound.	Conc./mol · L ⁻¹	$R_s/\Omega \cdot \text{cm}^2$	$Y_o \times 10^{-6}/\mu\Omega^{-1} \cdot \text{s}^n$	$n \times 10^{-3}$	$R_{ct}/\Omega \cdot \text{cm}^2$	$C_{dl} \times 10^{-4}/\mu\text{F} \cdot \text{cm}^{-2}$	θ	IE/%
HL ₁	Blank	13.42	373.9	753.5	119.6	1.3529	–	–
	1×10^{-6}	2.453	111.9	868.4	267.7	0.6575	0.5532	55.32
	3×10^{-6}	1.091	79.7	843.5	787.5	0.4866	0.8481	84.81
	5×10^{-6}	1.116	95.3	849.9	787.8	0.4425	0.8482	84.82
	7×10^{-6}	1.014	101.4	851.7	813.1	0.4366	0.8529	85.29
	9×10^{-6}	1.000	75.5	845.4	960.7	0.4299	0.8755	87.55
	11×10^{-6}	1.212	71.3	845.0	999.6	0.4287	0.8803	88.03
HL ₂	1×10^{-6}	10.160	110.2	803.1	177.7	0.8388	0.3269	32.69
	3×10^{-6}	9.449	123.4	794.9	182.5	0.7399	0.3446	34.46
	5×10^{-6}	9.504	148.8	807.5	189.3	0.7278	0.3682	36.82
	7×10^{-6}	13.460	328.1	776.3	194.0	0.4835	0.3855	38.35
	9×10^{-6}	11.600	257.6	807.6	206.4	0.3804	0.4205	42.05
	11×10^{-6}	12.430	264.1	813.7	222.2	0.3790	0.4617	46.17
	1×10^{-6}	12.803	536.8	670.5	120.9	1.3990	0.0107	1.07
HL ₃	3×10^{-6}	11.010	322.1	773.1	124.2	1.2520	0.0370	3.70
	5×10^{-6}	1.147	209.8	828.6	140.4	1.0101	0.1481	14.81
	7×10^{-6}	9.882	87.93	759.6	145.4	0.48805	0.1774	17.74
	9×10^{-6}	10.350	81.57	796.6	163.5	0.4876	0.2685	26.85
	11×10^{-6}	9.966	90.21	802.5	169.2	0.5679	0.293	29.31

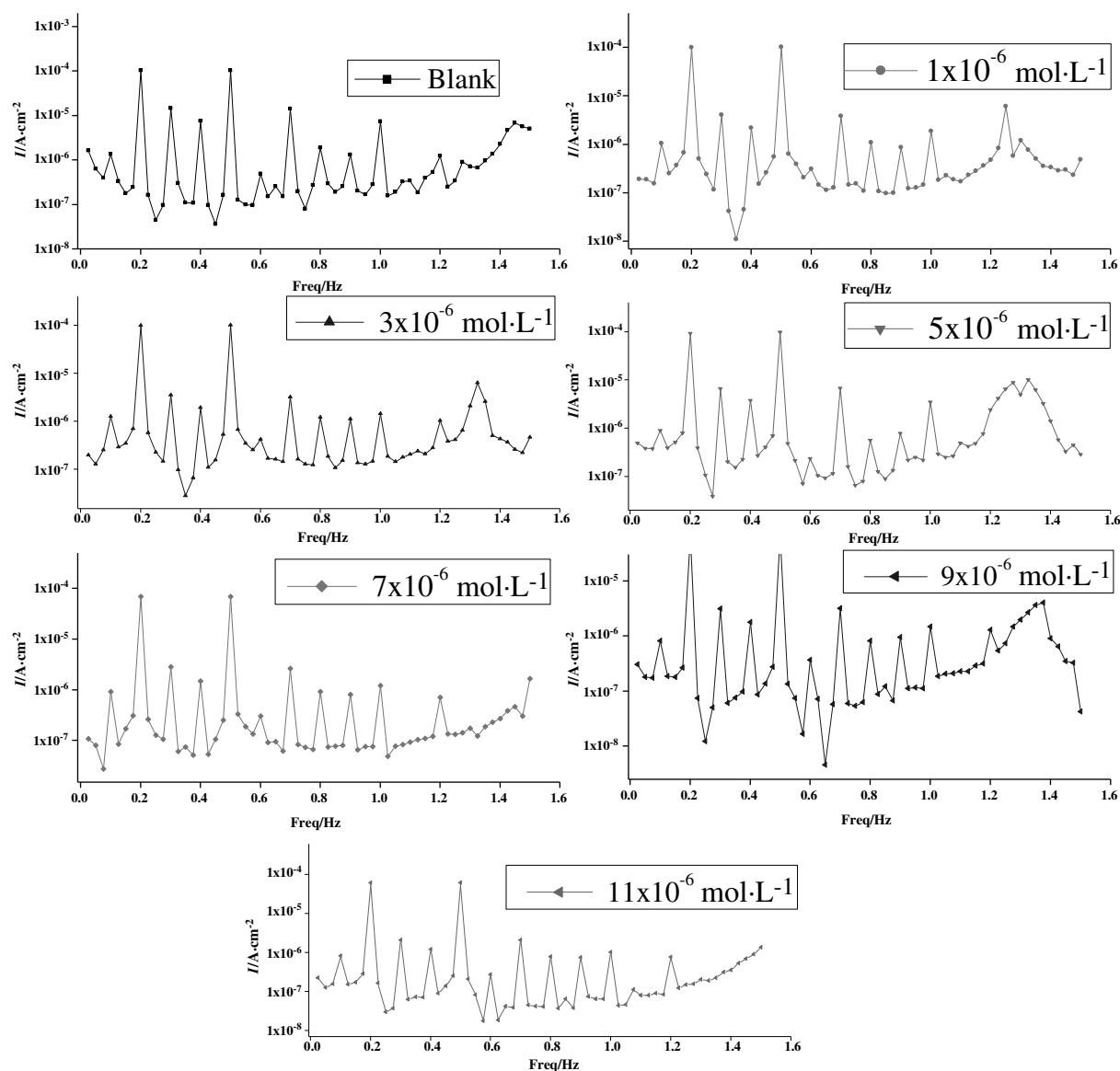


Fig. 8. EFM spectra for C-steel surface in hydrochloric acid in the absence and presence of different concentrations of compound HL_1 at $(30 \pm 1)^\circ\text{C}$.

to the different surface status of the electrode in two measurements. EIS was performed at the rest potential, while in polarization measurements the electrode potential was polarized to high over potential, non-uniform current distributions, resulted from cell geometry, solution conductivity, counter and reference electrode placement, etc., will lead to the difference between the electrode area actually undergoing polarization and the total area [45].

3.4. Electrochemical frequency modulation measurements

Bosch *et al.* recently proposed electrochemical frequency modulation (EFM) as a new electrochemical technique for online corrosion monitoring [46–48]. EFM is a rapid and nondestructive corrosion rate measurement technique that can directly give values of the corrosion current without prior knowledge of the Tafel constants.

In corrosion research, it is known that the corrosion process is non-linear in nature, a potential distortion by one or more sine waves will generate responses at more frequencies than the frequencies

of applied signal. Virtually, no attention has been given to the intermodulation or electrochemical frequency modulation. However, EFM showed that this non-linear response contains enough information about the corroding system so that the corrosion current can be calculated directly. The great strength of the EFM is the causality factors which serve as an internal check on the validity of the EFM measurement. With the causality factors the experimental EFM data can be verified.

Fig. 8 shows the current response contains not only the input frequencies, but also contains frequency components which are the sum, difference, and multiples of the two input frequencies.

The electrochemical corrosion kinetic parameters at different concentrations of inhibitors in $2 \text{ mol}\cdot\text{L}^{-1}$ HCl at 30°C were shown in Table 8. The inhibition efficiency was found to increase with increasing the inhibitor concentrations. The causality factors CF_2 and CF_3 in Table 8 are close to their theoretical values of 2.0 and 3.0, respectively indicating that the measured data are of good quality.

The calculated inhibition efficiency obtained from weight loss, Tafel polarization and EIS measurements are in good agreement with that obtained from EFM measurements, therefore IE tends to decrease in the following order:

Compound HL₁ > compound HL₂ > compound HL₃.

3.5. Quantum chemical calculations

Theoretical calculations were performed for only the neutral forms, in order to give further insight into the experimental results. Values of quantum chemical indices such as energies of LUMO and HOMO (E_{HOMO} and E_{LUMO}), and energy gap ΔE , are calculated by semi-empirical AM1, MNDO and PM3 methods that have been given in Table 9. The reactive ability of the inhibitor is related to E_{HOMO} and E_{LUMO} [49,50]. Higher E_{HOMO} of the adsorbent leads to higher electron donating ability [51]. Low E_{LUMO} indicates that the acceptor accepts electrons easily. The calculated quantum chemical indices (E_{HOMO} , E_{LUMO}) of investigated compounds are shown in Table 9. The difference in $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ is the energy required to move an electron from HOMO to LUMO. Low ΔE facility adsorption of the molecule and thus will cause higher inhibition efficiency.

The bond gap energy ΔE increases from compounds (HL₁ to HL₃). This fact explains the decreasing inhibition efficiency in this order ((HL₁) > (HL₂) > (HL₃)), as shown in Table 9, and Fig. 9 shows the optimized structures of the three investigated compounds. So, the calculated energy gaps show reasonably good correlation with the efficiency of corrosion inhibition. Table 9 also indicates that compound (HL₁) possesses the lowest total energy that means that compound (HL₁) adsorption occurs easily and is favored by the highest softness. The HOMO and LUMO electronic density distributions of these molecules were plotted in Fig. 9. For the HOMO of the studied compounds

that the benzene rings, N-atoms and O-atom have a large electron density. The data presented in Table 9 show that the calculated dipole moment decreases from compound HL₁ > compound HL₂ > compound HL₃.

3.6. Inhibition mechanism

Inhibition of the corrosion of C-steel in 2 mol·L⁻¹ HCl solution by some 8-hydroxy-7-quinolinecarboxaldehyde derivatives is determined by weight loss, potentiodynamic anodic polarization measurements, electrochemical impedance spectroscopy (EIS), and electrochemical frequency modulation method (EFM), it was found that the inhibition efficiency depends on concentration, nature of metal, the mode of adsorption of the inhibitors and surface conditions.

The observed corrosion data in the presence of these inhibitors, namely:

- the decrease of corrosion rate and corrosion current with increase in concentration of the inhibitor.
- the linear variation of weight loss with time.
- the shift in Tafel lines to higher potential regions.
- the decrease in corrosion inhibition with increasing temperature indicates that desorption of the adsorbed inhibitor molecules takes place.
- the inhibition efficiency was shown to depend on the number of adsorption active centers in the molecule and their charge density.

The corrosion inhibition is due to the adsorption of the inhibitors at the electrode/solution interface, the extent of adsorption of an inhibitor depends on the nature of the metal, the mode of adsorption of the inhibitor and the surface conditions. Adsorption on C-steel surface is assumed to take place mainly through the active centers attached to

Table 8

Electrochemical kinetic parameters obtained by EFM technique for C-steel surface in hydrochloric acid without and with various concentrations of 8-hydroxy-7-quinolinecarboxaldehyde derivatives (HL_n) at (30 ± 1)°C

Compound	Conc./mol·L ⁻¹	$i_{\text{corr}}/\mu\text{A}\cdot\text{cm}^{-2}$	$\beta_a \times 10^{-3}/\text{mV}\cdot\text{dec}^{-1}$	$\beta_c \times 10^{-3}/\text{mV}\cdot\text{dec}^{-1}$	CF-2	CF-3	IE/%
HL ₁	Blank	220.00	87.25	351.9	1.92	2.90	–
	1 × 10 ⁻⁶	24.01	115.50	242.2	1.55	2.88	89.08
	3 × 10 ⁻⁶	21.92	138.20	211.7	1.99	2.99	90.04
	5 × 10 ⁻⁶	18.45	112.70	189.1	1.96	3.10	91.61
	7 × 10 ⁻⁶	18.00	109.70	180.7	2.00	3.40	91.82
	9 × 10 ⁻⁶	14.53	90.94	134.3	2.03	2.98	93.39
	11 × 10 ⁻⁶	13.62	85.48	131.8	2.02	2.94	93.81
HL ₂	1 × 10 ⁻⁶	50.45	74.10	77.25	2.04	2.88	77.07
	3 × 10 ⁻⁶	36.68	105.6 0	190.0	1.93	3.27	83.33
	5 × 10 ⁻⁶	35.36	92.57	188.8	2.07	3.06	83.93
	7 × 10 ⁻⁶	32.44	96.23	191.2	2.02	1.95	85.25
	9 × 10 ⁻⁶	27.71	90.74	194.9	1.93	3.41	87.4
	11 × 10 ⁻⁶	26.95	91.51	164.5	1.92	2.76	87.75
	1 × 10 ⁻⁶	194.80	110.30	150.8	1.94	2.91	11.45
HL ₃	3 × 10 ⁻⁶	170.00	98.38	123.5	2.00	2.59	22.73
	5 × 10 ⁻⁶	167.00	90.76	149.8	1.85	2.49	24.09
	7 × 10 ⁻⁶	113.90	94.72	122.8	2.01	3.01	48.23
	9 × 10 ⁻⁶	101.00	86.03	114.9	1.92	2.75	54.09
	11 × 10 ⁻⁶	97.23	93.34	116.1	1.87	2.79	55.8

Table 9

The calculated quantum chemical properties for investigated compounds

Compound	$-E_{\text{HOMO}}$	$-E_{\text{LUMO}}$	ΔE	χ	η	σ	P_i	S^{-1}	ω	ΔN_{max}
HL ₁	0.18293	0.16915	0.0138	0.1760	0.0069	145.138	−0.1760	72.569	2.249	25.550
HL ₂	0.18701	0.16978	0.0172	0.1784	0.0086	116.077	−0.1784	58.038	1.8471	20.708
HL ₃	0.23677	0.17139	0.0654	0.2041	0.0327	30.591	−0.2041	15.295	0.6370	6.243

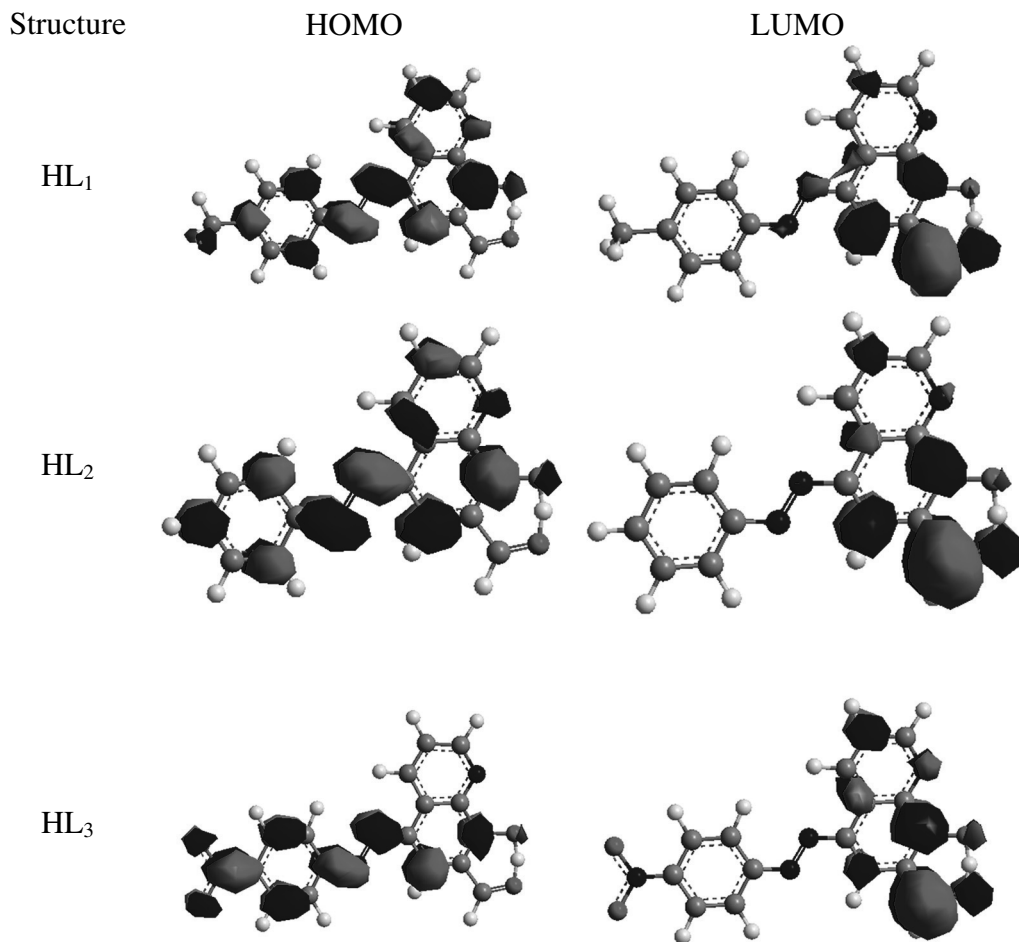


Fig. 9. The Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) of the investigated compounds.

the inhibitor and would depend on their charge density. The transfer of lone pairs of electrons on the oxygen atoms (CO/OH mode of the aldehyde and hydroxyl groups) [25] to the C-steel surface to form a coordinate type of linkage is favored by the presence of a vacant orbital in iron atom of low energy. Polar character of substituents in the changing part of the inhibitor molecule seems to have a prominent effect on the electron charge density of the molecule.

It was concluded that the mode of adsorption depends on the affinity of the metal towards the π -electron clouds of the ring system. Metals such as Cu and Fe, which have a greater affinity towards aromatic moieties, were found to adsorb benzene rings in a flat orientation. The order of decreasing the percentage inhibition efficiency of the investigated inhibitors in the corrosive solution was as follow:

Compound HL₁ > compound HL₂ > compound HL₃.

Compound HL₁ exhibits excellent inhibition power due to: (i) the presence of *p*-CH₃ group which is an electron donating group with negative Hammett constant ($\sigma = -0.17$), also this group will increase the electron charge density on the molecule, and (ii) its larger molecular size that may facilitate better surface coverage.

Compound HL₂ comes after compound HL₁ in inhibition efficiency. This is due to the fact that it has a lesser molecular size and has no substituent in *p*-position (H-atom with $\sigma = 0.0$) which contributes no charge density to the molecule.

Compound HL₃ comes after compound HL₂ in inhibition efficiency. This is due to the presence of *p*-NO₂ which has a positive Hammett constant ($\sigma = +0.78$) i.e. group which lowers the electron density on the molecule and hence, lower inhibition efficiency.

4. Conclusions

From the results of the study the following may be concluded:

- 1) Testing of azo 8-hydroxy-7-quinolinecarboxaldehyde derivatives establishes a very good inhibition for C-steel surface in hydrochloric acid solution.
- 2) The inhibition efficiency is in accordance to the order: compound HL₁ > compound HL₂ > compound HL₃.
- 3) The inhibition efficiencies of the tested compounds increase with increasing of their concentrations.
- 4) The adsorption of these compounds on C-steel surface in HCl solution follows a Langmuir adsorption isotherm.
- 5) The values of inhibition efficiencies obtained from the different independent techniques showed the validity of the obtained results.

References

- [1] M.A. Deyab, Effect of cationic surfactant and inorganic anions on the electrochemical behavior of carbon steel in formation water, *Corros. Sci.* 49 (2007) 2315–2328.
- [2] S.A. Abd El-Maksoud, A.S. Fouda, Some pyridine derivatives as corrosion inhibitors for carbon steel in acidic medium, *Mater. Chem. Phys.* 93 (2005) 84–90.
- [3] K.F. Khaled, Application of electrochemical frequency modulation for monitoring corrosion and corrosion inhibition of iron by some indole derivatives in molar hydrochloric acid, *Mater. Chem. Phys.* 122 (2008) 290–300.
- [4] E. Machnikova, K.H. Whitmire, N. Hackeman, Corrosion inhibition of carbon steel in hydrochloric acid by furan derivatives, *Electrochim. Acta* 53 (2008) 6024–6032.
- [5] H. Ashassi-sorkhabi, M.R. Magidi, K. Seyyedi, Investigation of inhibition effect of some amino acids against steel corrosion in HCl solution, *Appl. Surf. Sci.* 225 (2004) 176–185.
- [6] M.A. Migahed, I.F. Nassar, Corrosion inhibition of tubing steel during acidization of oil and gas wells, *Electrochim. Acta* 53 (2008) 2877–2882.

- [7] G. Avci, Corrosion inhibition of indole-3-acetic acid on mild steel in 0.5 mol·L⁻¹ HCl, *Colloids Surf. A* 317 (2008) 730–736.
- [8] M. Bagherzadeh, H. Haddadi, M. Iranpour, Electrochemical evaluation and surface study of magnetite/PANI nanocomposite for carbon steel protection in 3.5% NaCl, *Prog. Org. Coat.* 101 (2016) 149–160.
- [9] M. Abdallah, E.A. Helal, A.S. Fouda, Aminopyrimidine derivatives as inhibitors for corrosion of 1018 carbon steel in nitric acid solution, *Corros. Sci.* 48 (2006) 1639–1654.
- [10] A.S. Fouda, A.A. Al-Sarawy, E.E. El-Katori, Potentiometric and thermodynamic studies of 3-methyl-1-phenyl-[p-[N-(pyrimidin-2-yl)-sulfamoyl] phenylazo]-2-pyrazolin-5-one and its metal complexes, *Chem. Pap.* 60 (2006) 5–9.
- [11] O. Benali, L. Larabi, M. Traisnel, L. Gengembre, Y. Harek, Electrochemical, theoretical and XPS studies of 2-mercapto-1-methylimidazole adsorption on carbon steel in 1 mol·L⁻¹ HClO₄, *Appl. Surf. Sci.* 253 (2007) 6130–6139.
- [12] C. Verma, M.A. Quraishi, E.E. Ebenso, I.B. Obot, A. El-Assyry, 3-Amino alkylated indoles as corrosion inhibitors for mild steel in 1 mol·L⁻¹ HCl: Experimental and theoretical studies, *J. Mol. Liq.* 219 (2016) 647–660.
- [13] M.A. Khalifa, M. El-Batouti, F. Mahgoub, A.B. Akinish, Corrosion inhibition of steel in crude oil storage tanks, *Mater. Corros.* 54 (2003) 251–258.
- [14] H. Ashassi-Sorkhabi, B. Shaabani, D. Seifzadeh, Corrosion inhibition of mild steel by some Schiff base compounds in hydrochloric acid, *Appl. Surf. Sci.* 239 (2005) 154–164.
- [15] K.F. Khaled, The inhibition of benzimidazole derivatives on corrosion of iron in 1 mol·L⁻¹ HCl solutions, *Electrochim. Acta* 48 (2003) 2493–2503.
- [16] A. Popova, M. Christov, S. Raicheva, E. Sokolova, Adsorption and inhibitive properties of benzimidazole derivatives in acid mild steel corrosion, *Corros. Sci.* 46 (2004) 1333–1350.
- [17] R.E. Khidre, A.A. Abu-Hashem, M. El-Shazly, Synthesis and anti-microbial activity of some 1-substituted amino-4, 6-dimethyl-2-oxo-pyridine-3-carbonitrile derivatives, *Eur. J. Med. Chem.* 46 (2011) 5057–5064.
- [18] E.E. Ebenso, I.B. Obot, L.C. Murulana, Quinoline and its derivatives as effective corrosion inhibitors for mild steel in acidic medium, *Int. J. Electrochem. Sci.* 5 (2010) 1574–1586.
- [19] G. Achary, H.P. Sachin, Y.A. Naik, T.V. Venkatesha, The corrosion inhibition of mild steel by 3-formyl-8-hydroxy quinoline in hydrochloric acid medium, *Mater. Chem. Phys.* 107 (2008) 44–50.
- [20] V.R. Saliyan, A.V. Adhikari, Quinolin-5-ylmethylene-3-[(8-(trifluoromethyl) quinolin-4-yl) thio] propanohydrazide as an effective inhibitor of mild steel corrosion in HCl solution, *Corros. Sci.* 50 (2008) 55–61.
- [21] B.M. Mistry, S. Jauhari, Synthesis and evaluation of some quinoline Schiff bases as a corrosion inhibitor for mild steel in 1 mol·L⁻¹ HCl, *Res. Chem. Intermed.* 39 (2013) 1049–1068.
- [22] A.Z. El-Sonbati, M.A. Diab, A.A. El-Bindary, G.G. Mohamed, Sh.M. Morgan, M.I. Abou-Dobara, S.G. Nozha, Geometrical structures, thermal stability and antimicrobial activity of Schiff base supramolecular and its metal complexes, *J. Mol. Liq.* 215 (2016) 423–442.
- [23] A.Z. El-Sonbati, A.A. El-Bindary, Stereochemistry of new nitrogen containing aldehydes. V. Novel synthesis and spectroscopic studies of some quinoline Schiff bases complexes, *Pol. J. Chem.* 74 (2000) 621–630.
- [24] A.Z. El-Sonbati, A.A. El-Bindary, A.F. Shoaib, R.M. Younes, Stereochemistry of new nitrogen containing heterocyclic aldehyde. VII. Potentiometric, conductometric and thermodynamic studies of novel quinoline azo dyes and their metal complexes with some transition metals, *Chem. Pharm. Bull.* 49 (2001) 1308–1313.
- [25] N.A. El-Ghamaz, M.A. Diab, A.A. El-Bindary, A.Z. El-Sonbati, S.G. Nozha, Thermal, dielectric characteristics and conduction mechanism of azo dyes derived from quinoline and their copper complexes, *Spectrochim. Acta A* 143 (2015) 200–212.
- [26] Yu.P. Khodyrev, E.S. Batyeva, E.K. Badeeva, E.V. Platova, L. Tiwari, O.G. Sinyashin, The inhibition action of ammonium salts of O, O'-dialkyldithio-phosphoric acid on carbon dioxide corrosion of mild steel, *Corros. Sci.* 53 (2011) 976–983.
- [27] V.V. Torres, R.S. Amado, C.F. de Sá, T.L. Fernandez, C.A. Da Silva Riehl, A.G. Torres, E. D'Elia, Inhibitory action of aqueous coffee ground extracts on the corrosion of carbon steel in HCl solution, *Corros. Sci.* 53 (2011) 2385–2392.
- [28] T. Zhao, G. Mu, The adsorption and corrosion inhibition of anion surfactants on aluminium surface in hydrochloric acid, *Corros. Sci.* 41 (1999) 1937–1944.
- [29] M.J. Bahrami, S.M.A. Hosseini, P. Pilvar, Experimental and theoretical investigation of organic compounds as inhibitors for mild steel corrosion in sulfuric acid medium, *J. Corros. Sci.* 52 (2010) 2793–2803.
- [30] A. Ostovari, S.M. Hoseinie, M. Peikari, S.R. Shadizadeh, S.J. Hashemi, Corrosion inhibition of mild steel in 1 mol·L⁻¹ HCl solution by henna extract: A comparative study of the inhibition by henna and its constituents (lawsone, gallic acid, α-d-glucose and tannic acid), *Corros. Sci.* 51 (2009) 1935–1949.
- [31] M. Bouklah, B. Hammouti, M. Lagrenée, F. Bentiss, Thermodynamic properties of 2, 5-bis (4-methoxyphenyl)-1, 3, 4-oxadiazole as a corrosion inhibitor for mild steel in normal sulfuric acid medium, *Corros. Sci.* 48 (2006) 2831–2842.
- [32] F. Bensajjay, S. Alehyen, M. El Achouri, S. Kertit, Corrosion inhibition of steel by 1-phenyl 5-mercapto 1, 2, 3, 4-tetrazole in acidic environments (0.5 mol·L⁻¹ H₂SO₄ and 1/3 mol·L⁻¹ H₃PO₄), *Anti-Corros. Methods Mater.* 50 (2003) 402–409.
- [33] S.Z. Duan, Y.L. Tao, Interface Chem, Higher Education Press, Beijing, 1990 124–126 (in Chinese).
- [34] S.S.A. El-Rehim, S.A.M. Refaey, F. Taha, M.B. Saleh, R.A. Ahmed, Corrosion inhibition of mild steel in acidic medium using 2-amino thiophenol and 2-cyanomethyl benzothiazole, *J. Appl. Electrochem.* 31 (2001) 429–435.
- [35] K.K. Al-Neami, A.K. Mohamed, I.M. Kenawy, A.S. Fouda, Inhibition of the corrosion of iron by oxygen and nitrogen containing compounds, *Monatsh. Chem.* 126 (1995) 369–376.
- [36] 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.
- [37] J. Marsh, Advanced Organic Chemistry, third ed. Wiley Eastern, New Delhi, 1988.
- [38] S. Martinez, I. Stern, Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in the low carbon steel/mimosa tannin/sulfuric acid system, *Appl. Surf. Sci.* 199 (2002) 83–89.
- [39] H.M. Hassan, A.M. Eldesoky, R.M. Younis, W.A. Zordok, Density functional theory (DFT) studies on sulfa Dimedine azo derivatives as green inhibitors for C-steel in 0.5 mol·L⁻¹ H₃PO₄ solutions, *Int. J. Adv. Res.* 2 (2014) 550–568.
- [40] A.S. Fouda, A.M. Eldesoky, M.M. Muhtar, New cyanoacetamide derivatives as corrosion inhibitors for carbon steel in acidic media, *J. Adv. Chem.* 4 (2013) 323–350.
- [41] M. El Achouri, S. Kertit, H.M. Gouttaya, B. Nciri, Y. Bensouda, L. Perez, M.R. Infante, K. Elkacemi, Corrosion inhibition of iron in 1 mol·L⁻¹ HCl by some gemini surfactants in the series of alkanediyl-α, ω-bis-(dimethyl tetradecyl ammonium bromide), *Prog. Org. Coat.* 43 (2001) 267–273.
- [42] U. Rammelt, G. Reinhard, The influence of surface roughness on the impedance data for iron electrodes in acid solutions, *Corros. Sci.* 27 (1987) 373–382.
- [43] A. Le Mehaute, G. Grep, Introduction to transfer and motion in fractal media: The geometry of kinetics, *Solid State Ionics* 9–10 (1983) 17–30.
- [44] C.H. Hsu, F. Mansfeld, Technical note: Concerning the conversion of the constant phase element parameter Y0 into a capacitance, *Corrosion* 57 (2001) 747–748.
- [45] M. Lebrini, M. Lagrenée, M. Traisnel, L. Gengembre, H. Vezin, F. Bentiss, Enhanced corrosion resistance of mild steel in normal sulfuric acid medium by 2,5-bis(n-thienyl)-1,3,4-thiadiazoles: Electrochemical, X-ray photoelectron spectroscopy and theoretical studies, *Appl. Surf. Sci.* 253 (2007) 9267–9276.
- [46] H. Amar, A. Tounsi, A. Makayssi, A. Derja, J. Benzakour, A. Outzourhit, Corrosion inhibition of Armco iron by 2-mercaptobenzimidazole in sodium chloride 3% media, *Corros. Sci.* 49 (2007) 2936–2945.
- [47] K.F. Khaled, New synthesized guanidine derivative as a green corrosion inhibitor for mild steel in acidic solutions, *Int. J. Electrochem. Sci.* 3 (2008) 462–475.
- [48] K.F. Khaled, Molecular simulation, quantum chemical calculations and electrochemical studies for inhibition of mild steel by triazoles, *Electrochim. Acta* 53 (2008) 3484–3492.
- [49] A.S. Fouda, A.M. Eldesoky, A.Z. El-Sonbati, S.F. Salam, Prop-2-en-1-one derivatives as corrosion inhibitors for copper in 1 mol·L⁻¹ HNO₃, *Int. J. Electrochem. Sci.* 9 (2014) 1867–1891.
- [50] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B* 37 (1988) 785–789.
- [51] R.M. Issa, M.K. Awad, F.M. Atlam, Quantum chemical studies on the inhibition of corrosion of copper surface by substituted uracils, *Appl. Surf. Sci.* 255 (2008) 2433–2441.