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Synthesis and characterization of novel Cu (II) and Zn (II) complexes of 5-{[(2-Hydroxyethyl) sulfanyl] methyl}-8-hydroxyquinoline as effective acid corrosion inhibitor by Experimental and Computational testings

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Abstract

Two new complexes were synthesized, characterized and tested as inhibitors for mild steel corrosion in 1.0 M HCl. The anticorrosive effect has been studied using the potentiodynamic polarization (PDP) and impedance spectroscopy (EIS). The inhibitory efficiency increases with increasing concentration to reach 96.0% for Q-Cu and 94.6% for Q-Zn at 10⁻³ M. The two inhibitors are mixed type and follows the Langmuir isotherm adsorption. The surface of the mild steel has been examined by SEM/EDS and the corrosive solution by ICP-OES. DFT calculations and molecular dynamic simulation (MD) show a good correlation with the experimental results for both complexes.

Keywords: Synthesis; Complexes; Electrochemical techniques; ICP-OES/SEM; DFT/MD simulations.

1. Introduction

Organic synthesis attracted considerable attention because this procedure is suitable for the production of new polyfunctional heterocyclic compounds [1-3]. The objective of productions of heterocyclic compounds to be the subject of two considerations: the first consideration is to enrich the heterocyclic chemotherapy, the second consideration of increasing the applications of heterocyclic compounds to a broader spectrum [4]. The use of heterocyclic compounds has become widespread in several application fields such as biological, electrochemical, analytical and pharmaceutical field [5-8]. Today, researchers in this field making a shift from synthesis of classical organic compounds towards the synthesis of organic compounds that

meets modern application. Among these compounds, metal complexes were on top. The metal complexes have a multi-purpose use for example in metallurgy for precipitation or maintenance of a species in a solution [9], photography [10], recovery of noble metals [11], pigment staining [12], electroplating bath and antitumoral chemistry [13,14].

Today, several industries face major corrosion problems, particularly the ones operating in acidic environments such hydrochloric acid [15]. In order to mitigate this problem, several researchers have been proposed the protection of metals by chemical inhibitors because this method is more efficient and economical, especially the protection by organic inhibitors, because it is less toxic than inorganic inhibitors [16]. Among the organic compounds that are used for the protection of metals, we find the 8-hydroxyquinoline and its derivatives have the potentials to act as the corrosion inhibitors. The 8-hydroxyquinoline derivatives have been presented in several scientific publications as inhibitors for corrosion of metals in different acid and neutral media [17-20].

The investigations of the molecular properties related to the corrosion inhibition performances of the inhibitor molecules are performed by the quantum chemical calculations and molecular dynamics (MD) simulation. These two simulation techniques are very efficient among other available computer-aided-simulations [21-23]. With respect to quantum chemical calculation, inhibition effectiveness of the inhibitors can be determined by studying optimized geometries of the inhibitor molecules, electron distribution in the frontier molecular orbitals (FMOs) and adsorption related electronic properties *like* FMOs energies, energy gap, total energy and fraction of transferred electron between inhibitors and metal surfaces *etc*.

The obtained results provided by the above investigations have exuded more light on the active sites, inhibition mechanism and reactivity of the inhibitor molecules. However, the modern researchers have proposed that in order to predict the inhibition efficiency inherited by inhibitors, only quantum chemical approach cannot be sufficient enough [24,25]. It has

been found that the results obtain from DFT calculations cannot be correlated well with the experimentally obtained results in many cases [26,27]. In this purview, it is needed to emphasize the modelling of experimentation for the accurate prediction of chemical behavior and inhibition performance of the inhibitor molecules. A precise modelling of experimentation will take care of all concerned species (*like* H₂O, H₃O⁺, Cl⁻, Fe surfaces *etc.*) which actually take part in corrosion related process. In this perspective, in recent time, MD simulation is employed as a modern technique to envisage actual interfacial configuration of inhibitor molecules on the metal/solution interface [28,29].

This work aimed the preparation of new metal complexes based on 8hydroxyquinoline in order to enrich the library of heterocyclic compounds and to find the new physical-chemical, biological and electrochemical properties. The metal complexes were analyzed out by the following spectral methods: IR, NMR (¹H, ¹³C), EA and X-Ray. Also, these compounds were tested as a corrosion inhibitor of mild steel in 1.0 M HCl medium, Potentio-dynamic polarization (PDP), electrochemical impedance spectroscopy (EIS), density functional theory (DFT) and molecular dynamic simulation (MDS). The surface of the steel after corrosion test has been characterized by scanning electron spectroscopy (SEM) coupled with the energy dispersive spectroscopy (EDS), And the gravimetric solutions analyzed by the Inductively Coupled Plasma-Optical Spectroscopy (ICP-OES).

2. Materials and methods

2.1. Chemical study

2.1.1. Chemicals and equipment

All chemicals and materials used in this work followed international standards. The qualitative analysis of all the products synthesized in this work was carried out by the

following spectral methods: IR, NMR (¹H, ¹³C), EA and X-Ray. Further details concerning these materials and products have been published in another work [30].

The chemical compositions of the steel used in this work are: [Si (0.24); Mn (0.47); C (0.11); Mo (0.02); Ni (0.1); Cr (0.12); Al (0.03); Co (< 0.012); Cu (0.14); V (< 0.003); Fe (balance); W (0.06)]. Corrosive solutions were prepared from the dilution of a concentrated hydrochloric acid (37 %) with the distilled water (H₂O). The metal parts are cleaned with technical acetone and alcohol. The gravimetric tests were repeated three times for the reliability of the results.

2.1.2. Ligand Preparation

The ligand [5-{[(2-hydroxyethyl)sulfanyl]methyl}quinolin-8-ol] (**HL**) was synthesized in two steps; the first step consists of the conversion of 8-hydroxyquinoline (**HQ**) to 5-chloromethyl-8-hydroxyquinoline hydrochloride (**5-CMHQ**) by acid wading (HCl_g) at room temperature for 24 h. The second step is the reaction of the product **5-CMHQ** with the mercaptoethanol, in tetrahydrofuran (THF) in the presence of NaHCO₃ at reflux for 8 h (**Figure 1**).



Fig. 1. Ligand Preparation (HL)

2.1.3. Preparation of metal complexes

The metal complexes (Q-Cu and Q-Zn) were prepared by the reaction of the product HL with the zinc chloride or copper (II) chloride in ethanol (EtOH) in the presence of triethylamine (Et_3N) as a base at reflux for 3 h (Figure 2).



Fig. 2. Preparation of metal complexes (Q-Cu and Q-Zn).

2.2. Electrochemical study

The corrosion tests were carried out by the usual electrochemical methods such as electrochemical politicization and impedance spectroscopy. The details for electrochemical methods have been published in another publication [31].

Inhibitory efficiencies for gravimetric studies, polarization studies, and impedance spectroscopy, respectively, were designed using the following equations 1-3:

$$\eta_{\omega}(\%) = \frac{\omega_{corr}^{0} - \omega_{corr}}{\omega_{corr}^{0}} \times 100 \tag{1}$$

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

$$\eta_{\rm PP} = \frac{i_{\rm corr}^0 - i_{\rm corr}}{i_{\rm corr}^0} \times 100 \tag{2}$$

where i_{corr} and i_{corr}^0 are the corrosion current density with and without the addition of inhibitors.

The corrosion current density (i_{corr}) was calculated by extrapolating the linear Tafel segments of anodic and cathodic curves back to the corrosion potential

$$\eta_{\rm EIS} = \frac{R_{\rm p} - R_{\rm p}^0}{R_{\rm p}} \times 100 \tag{3}$$

where R_p and R_p^0 are the polarization resistance with and without the addition of inhibitors.

The gravimetric solutions have been investigated by the UV-visible spectrometry (UV-vis) and inductively coupled with plasma optical spectroscopy (ICP-OES). The metal surface was identified by the scanning electron microscope (SEM) connected with energy dispersive spectroscopy (EDS).

2.3. Details of DFT and MD simulation modeling methods

Theoretical methods, namely density functional theory (DFT) and molecular dynamics (MD) simulation, are the most commonly used approaches to explain the mode of action of an inhibitor on a metal support [32].

The DFT modeling of the **Q-Cu** and **Q-Zn** complexes have been accomplished by B3LYP hybrid functional to consider the electron exchange-correlation interactions. The interactions of copper and zinc atoms in the DFT calculations have been described by the effective potential of the core using the LanL2DZ base set [33]. The Gaussian 09 program was used to perform these DFT calculations [34]. When the calculation is completed, some important reactivity descriptors in quantum chemistry, namely E_{HOMO} (the energy of the highest occupied molecular orbital), E_{LUMO} (the energy of the lowest unoccupied molecular orbital), ΔE_{gap} (the energy difference), ΔN_{110} (the amount of the transferred electrons) and the total energy are calculated and interpreted [35-38].

The MD simulation cells adapted for the low interaction energy complex corrosion configurations of our studied complexes were constructed with consideration of the experimental conditions [39]. For this purpose, this dynamic simulation was carried out in an acidic medium. The vacuum created of 40 Å was filled with a solvent layer containing 500 water molecules, a molecule of complex optimized and minimized for at least 5000 steps using the smart algorithm for each simulation and 5 Cl⁻ and 5 H₃O⁺ corrosive ions. Thereafter, the constructed cells of $32.27 \times 32.27 \times 30.13$ Å³ size and of 13×13 unit were exposed to 400 ps with the NVT ensemble simulations which were run at 298 K using the Forcite module

which is adopted in the Materials Studio software suite. The COMPASS force field was selected to model the energies of Fe (110) atoms, water molecules, corrosive ions and **Q-Cu** or **Q-Zn** [40-42].

The interaction ($E_{interaction}$) and binding ($E_{binding}$) energies of **Q-Cu** and **Q-Zn** complexes in relation to Fe (110) surface in HCl medium are calculated as follows [43]:

(4)

(5)

 $E_{\rm interaction} = E_{\rm total} - E_{\rm surface+solution} - E_{inhibitor}$

 $E_{binding} = -E_{interaction}$

3. Results and Discussions

3.1. Chemical study

General procedures for ligand preparation (HL)

In a 100 mL flask, containing 40 mL of THF, 0.01 mol of *5-chloromethyl-8-hydroxyquinoline hydrochloride* **5-CMHQ** and 0.01 mol of mercaptoethanol (C₂H₆OS) were added in the presence of 0.01 mol NaHCO₃. The reaction mixture was refluxed with stirring for 8 h and then separated by a *TLC* plate. The reaction mixture was concentrated under vacuum and then extracted with dichloromethane. The resulting residue was purified by silica column chromatography (CH₂Cl₂: C₆H₁₄ = 85:15). **Yield:** 85 %; mp 110-112 °C; **F**_r 0.67; **Aspect**; White crystal; **IR** 1625,62 (C=C), 3239.18 (OH), 2036.29 (CH₂), 2398.10 (C=N). ¹**H** NMR: $\delta_{ppm} = 1.01$ (s, 2H, CH₂-C), 4.72 (s, 2H, CH₂-S), 6.99 (s, 1H, OH-Ar), 4.83 (s, 1H, OH), 7.01-7.34-7.56-8.83-9.77 (m, 5 H, ArH_{quinoline}). ¹³**C** NMR: $\delta_{ppm} = 153.21$ (C-OH-Ar), 34.28 (CH₂-S), 61.28 (CH₂-OH), 32.80 (C-C), 110.62-121.92-124.73-128.94-148.29 (ArCH_{quinoline}), 133.75-139.49 (ArCquinoline). **Elemental Analysis**: Molecular Formula: C₁₂H₁₃NO₂S (M = 235). **Calculated:** C, 61.25 %; H, 5.57 %; N, 5.95 %. **Found:** C, 61.02 %; H, 5.70 %; N: 5.37 %.

X-Ray Crystal Structures Description of Ligand

A white colored crystal of dimensions $0.44 \times 0.43 \times 0.23 \text{ mm}^3$ of **HL** was chosen for an X-ray diffraction study. The single crystal X-ray diffraction data show that it crystallizes in a space group, P2₁/c. The crystal belongs to the monoclinic system with the following lattice parameters: a = 11.8362 (7) Å, b = 11.7958 (7) Å, c = 7.8459 (5) Å, β = 91.673 (1) (°) and its unit cell volume is 1094.96 (12) Å³. The details of the crystal data and structure refinement were given in Table 1. Moreover, the obtained molecular structure of the title compound was depicted as Fig. 3 shows.



Fig. 3. The title molecule with labeling scheme and 50% probability ellipsoids. The intramoleculart O—H…N hydrogen bond is shown by a dashed line.

Table 1

Crystallographic and refinement data for HL.

Crystal data	
Chemical formula	$\underline{C_{12}}\underline{H_{13}}\underline{NO_{2}}\underline{S}$
$M_{ m r}$	<u>235.29</u>
Crystal system, space group	Monoclinic, <u>P2₁/c</u>
Temperature (K)	<u>120</u>

<i>a</i> , <i>b</i> , <i>c</i> (Å)	<u>11.8362 (7)</u> , <u>11.7958 (7)</u> , <u>7.8459 (5)</u>
β (°)	<u>91.673 (1)</u>
$V(Å^3)$	<u>1094.96 (12)</u>
Ζ	<u>4</u>
Radiation type	<u>Μο Κα</u>
μ (mm ⁻¹)	<u>0.28</u>
Crystal size (mm ³)	$\underline{0.44} \times \underline{0.43} \times \underline{0.23}$
Data collection	
Diffractometer	Bruker Smart APEX CCD
Absorption correction	Multi-scan SADABS (Krause et al., 2015)
T_{\min}, T_{\max}	<u>0.86, 0.94</u>
No. of measured, independent and observed [$I \ge 2\sigma(I)$] reflections	<u>33009, 2961, 2797</u>
R _{int}	0.025
$(\sin\theta/\lambda)_{max}$ (Å ⁻¹)	0.687
Refinement	
$R[F^2> 2\sigma(F^2)], wR(F^2), S$	<u>0.032, 0.093, 1.05</u>
No. of reflections	<u>2961</u>
No. of parameters	<u>191</u>
H-atom treatment	Only H-atom displacement parameters refined
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	<u>0.56</u> , <u>-0.20</u>

General procedure for metal complexes (Q-Cu and Q-Zn)

0.02 mole of [5-{[(2-hydroxyethyl)sulfanyl]methyl}quinolin-8-ol] (**HL**) is dissolved in 50 mL of absolute ethanol in the presence of triethylamine (0.01 mole), and the mixture is then heated until the mixture is completely dissolved. After 30 minutes of heating with stirring, a solution containing 0.01 mole copper (II) chloride or zinc chloride was added dropwise with stirring until the appearance of the solid with a color change of the solution. Then, the mixture

is refluxed for 3h and then poured into 150 mL of cold water. The metal complex is thus formed, filtered under vacuum, washed with ethanol and dried in the oven.

Q-Zn Complex:

¹H NMR: $\delta_{ppm} = 3.70$ (s, 2 H, CH₂-OH), 2.27 (s, 2 H, CH₂-S), 3.36 (s, 1 H, OH), 3.77 (s, 2 H, Ar-CH₂-S), 6.97-7.52-7.57-7.61-7.64 (m, 5 H, ArH_{quinoline}). ¹³C NMR: $\delta_{ppm} = 162.83$ (C-O-Ar), 31.28 (CH₂-S), 36.20 (C-C), 113.70-121.71-123.98-129.72-135.14-139.11-149.58-151.29 (ArC_{quinoline}). EA: Molecular Formula: C₂₄H₂₄N₂O₄S₂Zn (M = 533.97). Calculated C, 53.98 %; H, 4.53 %; N, 5.25 %. Found C, 53.25 %; H, 4.07 %; N, 5.73 %.

Q-Cu Complex:

¹H NMR: $\delta_{ppm} = 3.82$ (s, 2 H, CH₂-OH), 2.29 (s, 2 H, CH₂-S), 3.33 (s, 1 H, OH), 3.85 (s, 2 H, Ar-CH₂-S), 7.11-7.14-8.28-8.81-8.83 (m, 5 H, ArH_{quinoline}). ¹³C NMR: $\delta_{ppm} = 164.05$ (C-O-Ar), 56.23 (CH₂-S), 53.58 (CH₂-OH), 21.44 (C-C), 115.44-122.19-124.41-129.73-134.01-134.33-136.53-155.02 (ArC_{quinoline}). EA: Molecular Formula: C₂₄H₂₄CuN₂O₄S₂ (M = 532.13). Calculated C, 54.17 %; H, 4.55 %; N, 5.26 %. Found C, 54.56 %; H, 4.51 %; N: 5.05 %.

3.2. Electrochemical studies

3.2.1. EIS studies

The EIS tests in the absence and in the presence of various concentrations of metal complexes (Q-Cu and Q-Zn) in the solution of 1.0 M HCl was carried out at 298 K. The representative of the Nyquist diagrams from this test, together with the fitted curve are shown in Fig. 4. Moreover, we also have represented the Bode Modulus plots and Bode phase angle of the Nyquist diagrams in Fig. 4. The curves in Figure 4 are not perfectly semicircular and show a compression state. The incompleteness of the semicircles can be ascribed to the roughness of the electrode's surface and their compression can be attributed to the time constant of the electrical double layer and the charge transfer reaction [44]. In addition, the slopes of the

Bode modulus plots (log|Z| versus log *f*) are not equal to -1 (Figure 4), which are usually observed for solid electrodes as a result of frequency dispersion of interfacial impedance. Moreover, as Fig.4 depicts, the changes of inhibitory concentrations are followed by the changes of the diameters for the semicircles compared to the blank solution; which means that a protective layer was formed and thickened on the surface. Figure 4 reveals that by increasing the concentration of the inhibitor to the corrosive solution, the absolute value of the impedance increases at lower frequencies. In other words, by increasing the inhibitory concentration, the protecting potential of the metallic surface was increased against corrosion by adsorbing the inhibitory molecules on the surface and creating a layer [45]. The single peak in the phase angle diagrams in Fig. 4 represents the existence of a time constant. The depressed semicircles are generally attributed to the frequency dispersion, arising from roughness and inhomogeneity of the electrode's surface [44]. So, in such cases a constant phase element (CPE) is used instead of a pure capacitor to compensate for a non-ideal capacitive response of the interface to get a more fit to the experimental data and the impedance is given by Eq. 6:

$$Z_{\rm CPE} = Q^{-1} (i\omega)^{-n} \tag{6}$$

where Q is the proportionality coefficient (in $\Omega^{-1}s^n \text{ cm}^{-2}$), ω is the angular frequency and i is the imaginary number, n is the deviation parameter ($-1 \le n \le +1$) which has the meaning of a phase shift. When n =0 indicates the CPE represents a pure resistor, while n = -1 indicates the CPE represents an inductor and n = +1 indicates that the CPE represents a pure capacitor [45]. In this study, the best fit of the extracted experimental data is obtained for the equivalent circuit given in **Figure 4**. **Fig. 4** shows the electrical equivalent circuit diagram to model the mild steel/1.0 M HCl interface which consists of a *CPE*, polarization resistance (R_p), and solution resistance (R_s).

The impedance parameters from this figure (Figure 4) are collected in Table 2.



Fig. 4. EIS curves, Bode diagrams and Equivalent circuit for M-steel in 1.0 M HCl in the presence and absence of metal complexes Q-Cu and Q-Zn.

Table 2

The EIS parameters of MS before and after the addition of metal complexes (Q-Cu and Q-

Zn).

Medium	C (M)	$\begin{array}{c} R_{s} \\ (\Omega \ cm^{2}) \end{array}$	R_p ($\Omega \text{ cm}^2$)	C_{dl} (µF cm ⁻²)	n	$\begin{array}{c} Q \\ (\mu F S^{n-1}) \end{array} heta \end{array}$	$\eta_{ m EIS}$ %
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1.0 M HCl		1.12	34.7	121.0	0.773	419		
	10-6	0.9	351	84.9	0.783	231	0.901	90.1
	10-5	1.6	522	65.3	0.856	223	0.933	93.3
Q-Cu	10-4	1.2	610	33.7	0.814	195	0.943	94.3
	10-3	1.3	714	15.9	0.844	159	0.951	95.1
	10-6	1.2	153	100.4	0.811	220	0.773	77.3
	10-5	1.0	226	93.2	0.800	204	0.846	84.6
Q-Zn	10-4	1.0	238	84.8	0.808	196	0.854	85.4
	10-3	1.4	642	59.4	0.841	100	0.946	94.6

As per data in **Table 2**, it is observed that the surface coverage increases with increasing the inhibitory concentrations, which is due to the increase in the adsorption capacity of the inhibitors on the mild steel surface. In fact, the formation of a protective layer on the surface and the blocking of the active sites on the surface can be speculated accordingly. Moreover, it is observed that by increasing the concentration of inhibitors in the corrosive solution, the value of R_p is increased, while that of C_{dl} is decreased. This behavior is probably due to the adsorption of inhibitory molecules on the metallic surface and the decrease in the local dielectric constant, i.e. absorption of the inhibitor on the metallic surface reduces the electrical capacity by replacing the water molecules and other adsorbed ions on the surface [46,47]. The values of the index "*n*" close to unity show that the inhomogeneity of the surface has been increased by the adsorption of the two new complexes on the metallic surface [48]. The data about impedance showed that inhibitory efficacy increases from 90 % to 95 % by increasing the concentration of Q-Cu from 10⁻⁶ to 10⁻³ M.

3.2.2. Polarization studies

The polarization study is useful to obtain information on the kinetics of the substrate/inhibitor system on the slow stage. The polarization is distinguished by two main reactions such as in the anodic domain (iron oxidation) and in the cathodic domain (reduction of H^+).

$$Fe \leftrightarrow Fe^{2^+} + 2e^- \tag{7}$$

$$2H^+ + 2e^- \leftrightarrow H_2 \tag{8}$$

The electrochemical parameters of the steel extracted from the polarization curves (Figure 5) are given in Table 3.



Fig. 5. Polarization curves before and after the addition of metal complexes Q-Cu and Q-Zn.

Table 3

Polarization parameters of MS before and after the addition of metal complexes (Q-Cu and

Q-Zn).

Medium	Conc.	E _{corr}	<i>i_{corr}</i>	β _c	$\eta_{ m PP}$
	М	mV/Ag/AgCl	μA cm ⁻²	mV dec ⁻¹	%
1.0 M HCl	_	-498	983	-140	
	10-6	-525	86	-130	91.2
0.04	10-5	-542	62	-125	93.6
Q-Cu	10-4	-540	47	-120	95.2
	10-3	-552	36	-106	96.3
	10-6	-541	218	-135	77.8
Q-Zn	10-5	-545	150	-132	84.7
	10-4	-541	140	-130	85.7
	10-3	-525	52	-124	94.7

The polarization studies show that both complexes have a protective effect on the corrosion of MS. This inhibitory effect can be justified by the decrease in the values of the corrosion current intensity (i) after the addition of the two metal complexes to the corrosive solution. The inhibitory efficiency increases with increasing the concentrations of the complexes up to

an optimal value of 96 % for the complex **Q-Cu**. After the addition of the two complexes, it is noted that there is a slight decrease in the value of the potential and in the cathodic slopes with respect to the blank solution. This shows the mixed reactivity character of the two complexes with the steel surface [49]. According to **Table 3**, the corrosion potential, as shown in **Fig. 5**, changes to negative values by increasing the concentration of inhibitors, but this potential change is less than 85 mV. In addition, increasing the concentration of the inhibitors (**Q-Cu** and **Q-Zn**) in the corrosive solution causes the displacement of both anodic and cathodic branches. Therefore, these two inhibitors can be classified in the category of mixed inhibitors based on research done by other groups [50,51].

It is very clear from the **Table 3** that the presence of **Q-Cu** and **Q-Zn** in the 1.0 M HCl solution affects the values of the Tafel slopes. However, it is noticed that the change in β_c values of the inhibited systems with respect to that of the blank is independent of inhibitory concentration, that is, there is no pattern in β_c values of the inhibited solution with respect to that of the blank as increasing the concentration of **Q-Cu** and **Q-Zn**. This means that the kinetics of the cathodic reactions are not affected and the inhibition is by a simple geometric blocking mechanism [49].

In this study, the copper complex **Q-Cu** is more effective in the corrosion inhibition than the zinc complex **Q-Zn**, which can be explained by the electronegativity of copper is greater than that of zinc (χ_{Cu} = 1.69 > χ_{Zn} = 1.65). In addition, the results obtained by the study of the potentiodynamic polarization (*PDP*) confirm the results of impedance spectroscopy (*EIS*).

3.2.3. Temperature effect on corrosion process and activation parameters

For more than a century, scientists have been interested in the study of the corrosion of steels as a function of temperature, since temperature is essential for measuring the degree of protection of chemical inhibitors for steel surfaces [52]. The electrochemical data as a function of temperature are shown in Table 4 and Figure S2.

The inspection of both **Table 4** and **Figure S2** apparently indicates that an increase in temperature causes an increase in the values of the current density (i_{corr}) if adding the two complexes. Although there is a decrease in their inhibitory efficiencies, both inhibitors remain effective at high temperatures. Therefore, the temperature effect confirms that both complexes have a corrosion inhibiting effect even at high temperature. However, the study suffers from possible imprecision on the parameters of activation of corrosive reaction processes, for example, activation energy (E_a), activation enthalpy (ΔH_a) and activation entropy (ΔS_a).

The three activation parameters were calculated and compiled by the following Eqs. 9 and 10 [53]:

$$i_{corr} = A \exp\left(\frac{-E_a}{RT}\right)$$

$$i_{corr} = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(\frac{-\Delta H_a}{RT}\right)$$
(10)

The variation of Ln $(i_{corr}) = f$ (1/T) gives the activation energy value (E_a) (Figure S3A). The extrapolation of the Arrhenius equation and the variation of Ln $(i_{corr}/T) = 1000/T$ (Figure S3B) give the values of the activation enthalpy (ΔH_a) and the activation entropy (ΔS_a) . These three parameters [(E_a) , (ΔH_a) and (ΔS_a)] are gathered in Table S1.

From this data (**Table S1**), we can see that the activation energy (E_a) of both complexes **Q-Cu** and **Q-Zn** is greater than that of the blank solution. This shows that the inhibitors cause the formation of electrostatic fields (energy barrier) between the inhibitors and the steel surface [54]. The recent study about the temperature effect has also showed that the values of activation enthalpy (ΔH_a) for **Q-Cu** and **Q-Zn** are more positive than that for the blank solution. This indicates that **Q-Cu** and **Q-Zn** both increase the energy barrier of the corrosion of MS in 1.0 M HCl [55]. The values of the activation entropy (ΔS_a) for **Q-Cu** and **Q-Zn** are more positive than that for the control solution. This confirms that the two complexes **Q-Cu** and **Q-Zn** are adsorbed well to the surface of the steel. This is in good agreement with the literature [56].

3.2.4. Adsorption isotherm model study

The investigation about the adsorption isotherm is a continuing essential to identify the mode of protection of steels by the chemical inhibitors [57]. As well, knowledge of the types of interactions of the inhibitor in the system, inhibitor/metal surface/HCl is thus very important. After plotting the data from the EIS methods, the regression coefficient (R²) for Langmuir isotherm was very close to 1. Also, the slopes of the two straight lines for the two metal complexes (Q-Cu and Q-Zn) are also tending towards unity, suggesting that adsorption of inhibitors on the metal surface follows the Langmuir adsorption isotherm. The adsorption parameters are shown in Table S2 and Figure S4.

In this study, we tested several isotherms but the best isotherm was found to be the Langmuir isotherm (R^2 is approximately unity) [58]. The adsorption parameters extracted in this study are collected by the following equations [59]:

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}}{RT}\right)$$
(11)

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$
(12)

where θ , C_{inh} and K_{ads} are the fraction of the surface covered by the inhibitor, the concentration of the inhibitor and the adsorption constant, respectively.

Reports from other researchers show that if ΔG_{ads}° is more negative than $-20 \frac{kJ}{mol}$ means the physical absorption of the inhibitor occurs on the surface. This kind of absorption occurs due to the electrostatic reaction between the inhibitory molecules and the metallic surface. While if ΔG_{ads}° is less negative than $-40 \frac{kJ}{mol}$ shows a charge transfer occurs from the inhibitory

molecules to the metallic surface, the inhibitor adsorb on the metallic surface by the chemical absorption. Moreover, if ΔG_{ads}° has a value between $-40 \frac{kJ}{mol}$ and $-20 \frac{kJ}{mol}$, the adsorption of the inhibitor on the surface is a mixture of the physical and chemical absorption [60-62]. As listed in **Table S2**, it can be seen that the values of the adsorption free energy of the two complexes are greater than $-40 \frac{kJ}{mol}$. These results show that both inhibitors adsorb to the surface of the steel by chemical bonds, which confirms the good resistance at high temperature. The data of the adsorption isotherm showed that both complexes were good corrosion inhibitors for M-steel (*MS*) in 1.0 M HCl. This confirms that the results obtained in the polarization study, impedance spectroscopy, temperature effect and activation study.

3.2.5. ICP-OES analysis

In order to measure the amount of dissolved irons in the corrosive solution before and after the addition of the tested complexes (**Q-Cu** and **Q-Zn**), we performed an ICP-OES analysis [63]. In the case of irons in the corrosive solution, the amount of dissolved irons is only in the order of 250.569 mg/L. On the other hand, in the presence of both complexes, the amount of dissolved irons has been decreased to 5.089 mg/L for the **Q-Cu** complex and 6.058 mg/L for the **Q-Zn** complex. The ICP-OES analysis showed that our complexes have an excellent inhibitory effect on ordinary steel in molar hydrochloric acid.

3.2.6. Surface analysis (SEM and EDS)

To evaluate the degree of protection of the MS surface by the two tested complexes (**Q-Cu** and **Q-Zn**), we carried out a scanning electron spectroscopy analysis [64]. The immersion of the ironic substrate in molar hydrochloric acid for 6 hours shows that the surface of the M-steel was destroyed by corrosion (**Fig. 6A**). While, in the case of adding the tested complexes (**Q-Cu** and **Q-Zn**) in the corrosive solution, it is observed that the MS surface becomes to be well protected (**Fig. 6B, C**). The scanning electron microscope analysis also showed that our

complexes have a corrosion inhibiting effect for M-steel (MS) in 1.0 M HCl. The surface images in the presence of the tested complexes (**Q-Cu** and **Q-Zn**) are in the form of clouds. This can be explained by the presence of copper (Cu) and zinc (Zn) atoms will move when the current passes through them (the two complexes are semi-conductors).

The EDS spectra showed that in the case of addition of the complexes **Q-Cu** and **Q-Zn** (Fig. 6B and C), there are the presence of carbon (C), oxygen (O), nitrogen (N), copper (Cu) and zinc (Zn) atoms. In addition, in the case of adding the tested complexes (Fig. 6B and C), the percentage of dissolved irons was reduced compared to the blank surface (Fig. 6A). This confirms the presence of the tested complexes (**Q-Cu** and **Q-Zn**) on the surface of the steel.







Fig. 6. SEM image and EDS spectra of surface (MS) after immersion in 1.0 M HCl for 6 h without inhibitor (**A**), and with 10⁻³ M inhibitor (**B**) **Q-Cu** and (**C**) **Q-Zn**.

3.3. The DFT study

The electronic properties of **Q-Cu** and **Q-Zn** complexes were explored using the DFT method [23]. The optimized structures of these complexes are represented in top and side views in **Figure 7**. The two optimized complexes shown in **Figure 7** are in the minimum on the potential surface, which is proven by the positive values of the frequencies. Visual findings

showed that the **Q-Cu** geometry is almost planar around the copper, indicating that this element stabilizes both ligated quinolines. While in the presence of Zn, the geometry of the **Q-Zn** structure is non-planar, with the two quinolines were almost perpendicular to each other. In addition, the comparison revealed that the computed vibrational frequencies at B3LYP/LanL2DZ showed acceptable deviations from the experimental results (**Figure S1**). Indeed, this result showed that the complexes obtained are well identified theoretically and experimentally.



Fig. 7. Optimized structures of Q-Cu and Q-Zn complexes represented in top and side views.

The bond lengths, bond and dihedral angles of the optimized complexes appeared in Figures 8 and 9, respectively. As depicted in Figure 8, the bond lengths between the heteroatoms (O and N) and the metal in the Q-Cu complex (1.97-1.98 Å) were smaller than those in the Q-Zn complex (1.97-2.12 Å). This result indicates that the stability of the Q-Cu complex is higher than that of the Q-Zn complex. In addition, the comparison showed the bond lengths in the complexed quinoline ligands were the same as those in the uncomplexed ones. The complexation doesn't significantly affect the geometry of quinoline and only influence the heteratom-metal distance. The change in the geometry caused by the complexation is also justified by the values of bond and dihedral angles as shown in Figure 9.



Fig. 8. Calculated bond angles descriptors of Q-Cu and Q-Zn at the B3LYP /LanL2DZ theoretical level.



Fig. 9. Calculated dihedral angles of *Q-Cu* and *Q-Zn* at the B3LYP/LanL2DZ theoretical level.

For the purpose of clarifying the adsorption mechanism of the two metal complexes, namely **Q**-**Cu** and **Q-Zn**, on the MS surface in 1.0 M hydrochloric acid, we were very interested in investigating the electron density distribution of frontier molecular orbitals (FMOs) (HOMO and LUMO) (**Figure 10**) to predict the spatial disposition of these orbitals in which the type(s) of atoms that are responsible for corrosion inhibitory reactivity [65,66]. Indeed, the overall visual analysis of the electron density of HOMOs and LUMOs indicates that they are distributed over the atoms on the skeletions of quinolines in the studied complexes. Therefore, this distribution of FMOs showed that the tested complexes carry electron donating and accepting sites, reinforcing the adsorption of these species on the iron metal surface [67]. Specifically, it is clear that the **Q**-**Cu** complex is characterized by two distributions of electronic densities of frontier molecular orbital densities (FMOs) such as alpha FMOs (spin up) and beta FMOs (spin down). This behavior is possibly due to the presence of the copper (Cu) element that is responsible for this separation of spins. This produces a more active property of the **Q-Cu** complex with respect to the **Q-Zn**

complex. All these results can inform us that the two tested complexes adsorb on the iron surface by the skeleton of the quinoline in these complexes except the substituent (2-(methylthio)ethanol).



Fig. 10. Distribution of the FMO electron densities of the complexes using DFT with the B3LYP/LanL2DZ theoretical level.

Concerning the quantum chemical descriptors that are obtained from the graphical evaluations of FMO distributions, the energy values of HOMO (E_{HOMO}) and LUMO (E_{LUMO}) and their difference (ΔE_{gap}) allow a quantitative evaluation of the chemical reactivity of the selected complexes [68]. In general, the higher E_{HOMO} values of a molecule reflect a high electron donating power to another element that carries high electron deficiencies [69]. While a lower E_{LUMO} value of the same molecule implies that this molecule is capable of accepting more electrons [70]. And when the smaller energy gap reflects that the molecule studied is more reactive [71]. In addition, the fraction of the transferred electrons (ΔN_{110}) and total energy (E_T) were calculated for each inhibitory complex. All the values of these descriptors are summarized in **Table 4**. It is very notable from the results listed in this table that the **Q-Cu** complex had lower values of E_{LUMO} (-2.626 eV), ΔE_{gap} (2.689 eV) and E_T (-1555.648 au) with respect to the **Q-Zn** complex. These observations inform that **Q-Cu** is more reactive toward the iron metal surface with respect to the **Q-Zn**. While the high values of E_{HOMO} and ΔN_{110} of **Q-Cu** indicate that this complex shares more electrons with the surface of the iron substrate [72]. Therefore, **Q-Cu** inhibits corrosion more efficiently than **Q-Zn**. This result is logical because copper is a noble metal that effectively resists corrosion, whereas zinc is an active metal. Accordingly, **Q-Cu** complex is a good corrosion inhibitor.

Table 4

Complex	E _{HOMO}	E _{LUMO}	ΔE_{gap}	ΔN_{110}	E _T
	(eV)	(eV)	(eV)		(au)
Q-Cu($\alpha(spin \uparrow)$)	-5.365	-2.147	3.218	0.331	1555 (10
Q-Cu($\beta(\text{spin} \downarrow)$)	-5.315	-2.626	2.689	0.316	-1333.048
Q-Zn	-5.421	-2.188	3.233	0.314	-1425.116

Chemical quantum descriptors of Q-Zn and Q-Cu complexes in the gaseous state.

The active centers of two complexes were further investigated by using the Fukui functions Fukui(+) and Fukui(-) which provide a demonstration of nucleophilic and electrophilic interactions, respectively [73]. Table 5 represents all Fukui centers related to electrophilic/nucleophilic attacks of the tested complexes. Figure 11 shows the most relevant sites responsible for the interaction with the metal surface. As depicted in Figure 11, in the Q-Cu complex, the local reactivity is clearly defined by the oxygen atoms bound by the copper metal, i.e. O (11), O (22) and Cu (23) atoms play the important role as the sites responsible for electrophilic and nucleophilic attacks. This enhances the adsorption of the Q-Cu and Q-Zn complexes on the surface of the iron substrate. In addition, the copper atom has a high Fukui density, which indicates that this atom is considered a friendly element by iron atoms. Concerning the local reactivity of the active sites in Q-Zn, it is notable that the element zinc has no remarkable trend in Fukui density, which is why the inhibitory efficacy of

Q-Zn is lower than that of **Q-Cu**. In addition, the results shown in **Figure 11** and grouped in Table 6 show those oxygen atoms (O (11) and O (22)) and the appearance of new carbon atoms are responsible for the electrophilic attack.

Table 5. Fukui (+) and Fukui (-) of **Q-X** (X = Cu or Zn) complexes calculated at DFT/GGA/DNP using Material studio 2016.

Atoms	X = Cu		X = Zn	
1 1001115	Fukui(-)	Fukui(+)	Fukui(-)	Fukui(+)
C (1)	0.023	0.023	0.024	0.030
C(2)	0.029	0.029	0.046	0.029
C(3)	0.004	0.004	0.024	0.015
C (4)	0.005	0.005	0.012	0.014
C (5)	0.012	0.012	0.012	0.013
C (6)	0.027	0.027	0.050	0.021
N (7)	0.017	0.015	0.004	0.033
C (8)	0.021	0.022	0.022	0.040
C (9)	0.022	0.022	0.024	0.032
C (10)	0.030	0.031	0.022	0.061
0(11)	0.061	0.057	0.058	0.017
C (12)	0.023	0.023	0.024	0.030
C (13)	0.029	0.029	0.046	0.029
C (14)	0.004	0.004	0.024	0.015
C (15)	0.005	0.005	0.012	0.014
C (16)	0.012	0.012	0.012	0.013
C (17)	0.027	0.027	0.050	0.021
N (18)	0.017	0.015	0.004	0.033
C (19)	0.021	0.022	0.022	0.040
C (20)	0.022	0.022	0.024	0.032
C (21)	0.030	0.031	0.022	0.061
O (22)	0.061	0.057	0.058	0.017
X (23)	0.154	0.163	0.015	0.034
C (24)	0.003	0.023	0.026	0.013
S (25)	0.017	0.029	0.009	0.008
C (26)	0.008	0.004	0.004	0.003
C (27)	0.004	0.005	0.008	0.008
O (28)	0.007	0.012	0.005	0.002
C (29)	0.003	0.027	0.026	0.013
S (30)	0.017	0.015	0.009	0.008
C (31)	0.008	0.022	0.004	0.003
C (32)	0.004	0.022	0.008	0.008
O (33)	0.007	0.031	0.024	0.030



Fig. 11. Atom-condensed Fukui functions of **Q-Cu** and **Q-Zn** complexes calculated at DFT/GGA/DNP using Material studio 2016.

3.4. MD simulation

The molecular dynamics (MD) study was used to examine interactions at the interface between **Q-Cu** or **Q-Zn** and the contact surface Fe (110) [74]. In addition, based on the study of these interactions occurring at the interface, we have endeavored to explain the phenomenon of the adsorption of the complexes studied on the metallic surface [75]. Figure 12 showed the side/top views of the adsorption of the two inhibitory complexes on the first iron layer relative to the iron plane (110). Visual analysis of the images depicted in Figure 12

showed that the two Q-Cu and Q-Zn complexes adsorb on the iron surface in the same manner such that these two species are situated above Fe (110), which results in a large coverage of the metallic surface and thus has a high degree of corrosion inhibition performance [76]. In addition, it is evident that the copper element is very close to the iron atoms of the first layer than the zinc element, which shows that **Q-Cu** inhibits corrosion better than **O-Zn**. When the systems studied are in the most stable state, the energy values of the interaction energy (E_{interaction}) and binding energy (E_{binding}) can be extracted from these values and the inhibitory capacity of each complex against corrosion can be clarified. The simulation results showed that the interaction (binding) energy values of Q-Cu and Q-Zn are -229.127 (229.127) and -214.453 (214.453) kJ/mol, respectively. The more negative value of Einteraction and the more positive value of E_{binding} for **Q-Cu** inform that this complex reacts more strongly with the Fe (110) surface than Q-Zn [77]. This result is possibly proven that the copper atom interacts more effectively with iron atoms, indicating a better corrosion inhibitory performance. All these simulation results were in parallel with the experimentally-found order of the inhibitory efficacy for the studied complexes. The adsorption of Q-Cu and Q-Zn on Fe (110) was reinforced by inhibitor-Fe (110) interatomic bonds [78]. This phenomenon has been studied using the radial distribution function (RDF) method [78]. Figure 13 shows the variation of g(r) as a function of the atomic radius (inhibitor-Fe (110)) of the most active atoms (N7, O11, N18, O22, Cu and Zn) of the mentioned complexes and the atoms of the first iron layer. The values of bond lengths which were obtained from the most intense first peak for each spectrum, were noted in Figure 13. All these values were included in the chemisorption range (1 - 3.5 Å). As shown in Figure 13, it was very noticeable that the distance of Cu-Fe is smaller than that of Zn-Fe, which shows Q-Cu should adsorb more strongly on Fe (110) surface than Q-Zn. This behavior might promote the inhibitory efficacy of **Q-Cu**.



Fig. 12. Simulated adsorption configurations of **Q-Cu** and **Q-Zn** complexes over Fe (110) surface produced by MDs at 298 K.



Fig. 13. RDFs of Fe (110) surface relative to N7, O11, N18, O22, Cu or Zn atoms of **Q-Cu** and **Q-Zn** complexes at 298 K.

4. Conclusion

We conclude from our study that the two new metal complexes (Q-Cu and Q-Zn) are potential corrosion inhibitors for mild steel in molar hydrochloric acid environment (1.0 M HCl). The polarization (PDP) studies showed that both metal complexes (Q-Cu and Q-Zn) act on the surface of the steel as a mixed type inhibitor. However, from the aspect of thermodynamics, the adsorption and the activation studies showed that the two metal complexes (Q-Cu and Q-Zn) act on the **Zn**) adsorb on the MS surface by chemical approach with high resistance at high temperature (88 % for Q-Cu and 86 % for Q-Zn). The analysis of gravimetric solutions by Inductively Coupled Plasma-Optical Spectroscopy (ICP-OES) confirmed that our metal complexes (Q-Cu and Q-Zn) reduces the dissolution of iron in the corrosive medium. Analysis by the scanning electron microscope (SEM) connected with energy dispersive spectroscopy (EDS) showed that the two compounds strongly adsorbed on the MS surface. The theoretical calculations explained the adsorption process of the studied metal complexes (Q-Cu and Q-Zn) on the substrate surface.

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