



Some antipyrine derivatives as corrosion inhibitors for copper in acidic medium: Experimental and quantum chemical molecular dynamics approach

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Abstract

Schiff base of antipyrine derivatives namely, 4-(4-methoxy-benzalideneamine) antipyrine (I), 4-(4-benzalidene-amine) antipyrine (II) and 4-(4-nitro-benzalideneamine)antipyrine (III) have been investigated as corrosion inhibitors for copper in 2 M HNO₃ at different concentrations and 30±1 °C using chemical (weight loss) and electrochemical (Tafel polarization method, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM)) measurements. Generally, inhibition efficiency of the investigated compounds was found to depend on the concentration and the nature of the inhibitors. Quantum chemical calculation results show that the antipyrine ring and heteroatoms are the active sites of the three inhibitors. The adsorption behaviour of the studied inhibitors on copper surface has been studied using molecular dynamics (MD) method and density functional theory. The results indicated that the three antipyrine derivatives could adsorb on the copper surface firmly through the antipyrine ring and heteroatoms, the three inhibitors have excellent corrosion inhibition performance.

Keywords: Acid corrosion inhibition, Tafel, Quantum mechanics, antipyrine derivatives.

1-Introduction

Copper has electrical and thermal conductivities, good corrosion resistance and mechanical workability. It is widely used in heating and cooling systems. Corrosion of copper can lead to many problems, the most being per formation that may result in coolant leakage. Scales and corrosion products have negative influence on heat-transfer, causing a decrease in heating efficiencies of the copper structures [1]. Thus, corrosion of copper and its alloys and their inhibition in aqueous chloride solutions have attracted the attention of a member of investigators [2–6]. The use of organic inhibitors is one of the most practical methods for protection against corrosion of metals and their alloys. Generally, numerous organic compounds containing hetero atoms such as nitrogen [7–9], oxygen [10–13], phosphorus [14] and sulphur [15–18] are used as corrosion inhibitors. Studies of the relation between adsorption and corrosion inhibition are of considerable importance. In aqueous solutions, the inhibitory action of organic inhibitors is due to their physical (electrostatic) adsorption onto the metal surface, depending on the charge of the metal surface, the electronic structure of organic inhibitor and the nature of the medium [19–21]. Because of the fact that most of the chemical compounds that prevent the corrosion of metals and alloys are toxic, and thus pose threat both for human health and environment, their usage is limited. For this reason, several authors reported the use of natural products as corrosion inhibitors, also, some authors used drugs as green corrosion inhibitors for various metals and alloys [22–28].

The first objective of this work is to investigate the effect of the three antipyrine derivatives on the corrosion of copper in 2M HNO₃ using chemical and electrochemical methods. The second objective is to investigate the dependence of inhibition efficiency of these compounds on theoretical chemical parameters such as the energies of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO} ; net atomic charges, dipole moments.

2- Experimental detail

2.1- Composition of material samples:

Table 1: Chemical composition of the copper in weight %.

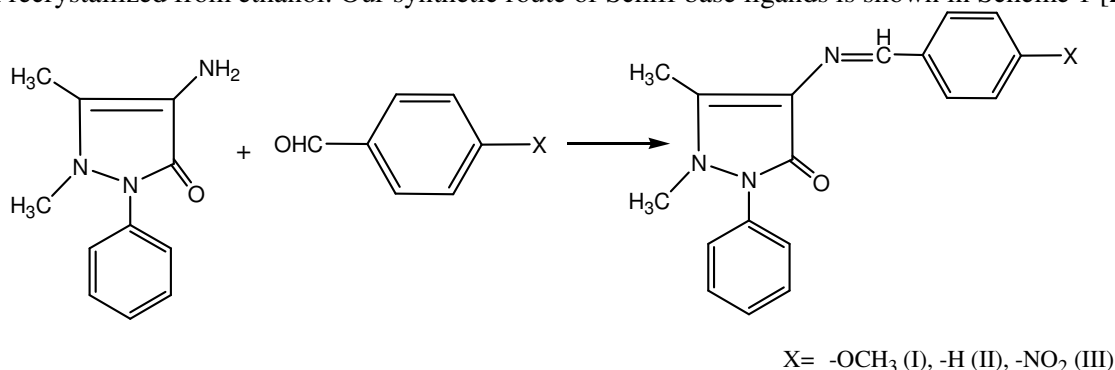
Element	Sn	Ag	Fe	Zn	Pb	As	Cu
Weight %	0.001	0.001	0.01	0.05	0.002	0.0002	The rest

2.2- Chemicals and solutions

Nitric acid (BDH grade) and organic additives

The organic inhibitors used in this study were some antipyrine derivatives, listed in Table (2).

Ethanol solutions of 4-aminoantipyrine (0.1 mol) and 4-derivatives benzaldehyde (0.1 mol) were refluxed together for 4 h over a steam bath. The excess solvent was removed by evaporation and the concentrated solution was cooled in an ice bath with stirring. The Schiff base (L_{I-III}) which separated out as a colored powder and then recrystallized from ethanol. Our synthetic route of Schiff base ligands is shown in Scheme 1 [29].



Scheme 1: Synthetic route of Schiff base ligands.

2.3. Methods used for corrosion measurements

2.3.1. Weight loss tests

For weight loss measurements, square specimens of size 2 cm x 2 cm x 0.2 cm were used. The specimens were first polished to a mirror finish using 400 and 800 grit emery paper, immersed in methanol and finally washed with bidistilled water and dried before being weighed and immersed into the test solution. The weight loss measurements were carried out in a 100 ml capacity glass beaker placed in water thermostat. The specimens were then immediately immersed in the test solution without or with desired concentration of the investigated compounds. Triplicate specimens were exposed for each condition and the mean weight losses were reported in order to verify reproducibility of the experiments.

2.3.2. Potentiodynamic polarization measurements

Polarization experiments were carried out in a conventional three-electrode cell with platinum gauze as the auxiliary electrode (1 cm²) and a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as reference electrode. The working electrode was in the form of a square cut from copper sheet of epoxy resin of polytetrafluoroethylene so that the flat surface area was 1 cm². Prior to each measurement, the electrode surface was pretreated in the same manner as the weight loss experiments. Before measurements, the electrode was immersed in solution at natural potential for 30 min. until a steady state was reached. The potential was started from - 600 to + 400 mV vs. open circuit potential (E_{ocp}). All experiments were carried out in freshly prepared solutions at 25 °C and results were always repeated at least three times to check the reproducibility.

2.3.3. Electrochemical Impedance Spectroscopy measurements

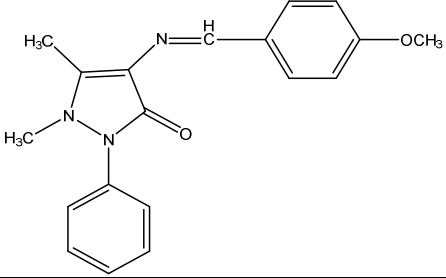
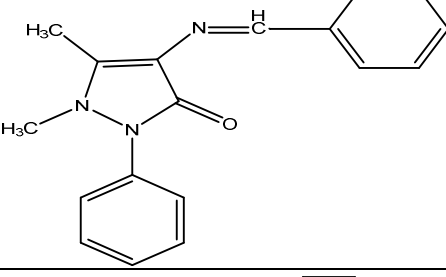
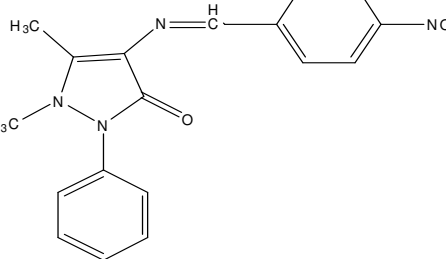
Impedance measurements were carried out using AC signals of 5 mV peak to peak amplitude at the open circuit potential in the frequency range of 100 kHz to 0.1 Hz. All impedance data were fitted to appropriate equivalent circuit using the Gamry Echem Analyst software.

2.3.4. Electrochemical Frequency Modulation technique

EFM experiments were performed with applying potential perturbation signal with amplitude 10 mV with two sine waves of 2 and 5 Hz. The choice for the frequencies of 2 and 5 Hz was based on three arguments [30]. The larger peaks were used to calculate the corrosion current density (i_{corr}), the Tafel slopes (β_c and β_a) and the

causality factors CF-2 and CF-3 [31]. All electrochemical experiments were carried out using Gamry instrument PCI300/4 Potentiostat/Galvanostat/Zra analyzer, DC105 corrosion software, EIS300 electrochemical impedance spectroscopy software, EFM140 electrochemical frequency modulation software and Echem Analyst 5.5 for results plotting, graphing, data fitting and calculating.

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

Compound No.	Structure	Name	Mol. Wt. / Mol. Formula
(I)		4-(4-methoxy-benzalideneamine)-antipyrine	321.0 / C ₁₉ H ₁₉ N ₃ O ₂
(II)		4-(4-benzalideneamine)-antipyrine	291.0 / C ₁₈ H ₁₇ N ₃ O
(III)		4-(4-nitro-benzalideneamine)-antipyrine	336.0 / C ₁₈ H ₁₆ N ₄ O ₃

2.3.5 .Theoretical study

Accelrys (Material Studio Version 4.4) software for quantum chemical calculations has been used.

3. Results and discussion

3.1. Weight loss measurements

Figure (1) represents the weight loss-time curves in the absence and presence of different concentrations of compound (I). Similar curves were obtained for other inhibitors (not shown).

$$\Delta W = W^0 - W_1 \quad (1)$$

where W^0, W_1 are the weight of the sample before and after immersion.

The degree of dissolution, of course, dependent on the surface area of the metal exposed and the time of exposure; hence the amount of corrosion is given with respect to area and time as shown in equation (2).

$$\%IE = [1 - (\Delta W_{inh} / \Delta W_{free})] \times 100 \quad (2)$$

Where W_{inh} and W_{free} are the weight losses in presence and absence of inhibitor, respectively.

The corrosion rate (C.R) was calculated from equation (3) as follows:

$$C.R. = \Delta W / At \quad (3)$$

Where ΔW is the weight loss in mg, A is the area in cm², t is the time in min.

Table (3) collects the values inhibition efficiency obtained from weight loss measurements in 2 M HNO₃ at 30 ± 0.1 °C. The results of this Table show that the presence of inhibitors reduces the corrosion rate of copper in 2 M HNO₃ and hence, increase the inhibition efficiency. The inhibition achieved by these compounds decreases in the following order: Compound (I) > Compound (II) > Compound (III).

3.2. Adsorption isotherm

It is widely acknowledged that adsorption isotherm provide useful insight onto the mechanism of corrosion inhibition as well as the interaction among the adsorbed molecules themselves and their interaction with the electrode surface [32]. In this study, Temkin adsorption isotherm was found to be suitable for the experimental results. The isotherm is described by the following equation:

$$\theta = 2.303/a \log K_{ads} + 2.303/a \log C \quad (4)$$

where C is the inhibitor concentration, K_{ads} is the adsorption equilibrium constant. The plot of θ versus $\log C$ was linear relation (shown in Figure (2)). And the adsorption equilibrium constant K_{ads} can be calculated from the intercept. Also ΔG°_{ads} can be calculated from the following equation:

$$\log K_{ads} = -\log 55.5 - \Delta G^\circ_{ads} / 2.303RT \quad (5)$$

where value of 55.5 is the concentration of water in solution in mole/liter [33], R is the universal gas constant and T is the absolute temperature. It was appear that the value of ΔG°_{ads} has a negative sign ensure the spontaneity of the adsorption and stability of the adsorbed layer on the alloy surface [34]. Also the values of ΔG°_{ads} around 40 kJ mol⁻¹ which was attributed to electrostatic interactions between inhibitors species and the charged metal surface (physisorption). From Table (4), the values of K_{ads} were found to run parallel to the % IE [$K(I) > K(II) > K(III)$]. This result reflects the increasing capability, due to structural formation, on the metal surface [35].

Table 3: Variation of corrosion rate (C.R) and inhibition efficiency (% IE) of the investigated compounds (I-III) with their molar concentrations at different temperatures from weight loss measurements at 120 min immersion in 2 M HNO₃ at 30 ± 0.1 °C.

Conc. (M)	Corrosion rate (CR) (mg cm ⁻² min ⁻¹) × 10 ⁻³			Inhibition efficiency (% IE)		
	(I)	(II)	(III)	(I)	(II)	(III)
1x10 ⁻⁶	19.08	21.27	22.00	51.55	46.00	44.14
3x10 ⁻⁶	16.46	18.26	18.88	58.20	53.64	52.06
5x10 ⁻⁶	14.71	17.15	17.91	62.65	56.47	54.53
7x10 ⁻⁶	13.66	16.05	16.97	65.32	59.26	56.91
9x10 ⁻⁶	12.45	15.31	16.45	68.39	61.11	58.24
11x10 ⁻⁶	11.24	14.09	15.60	71.46	64.23	60.39

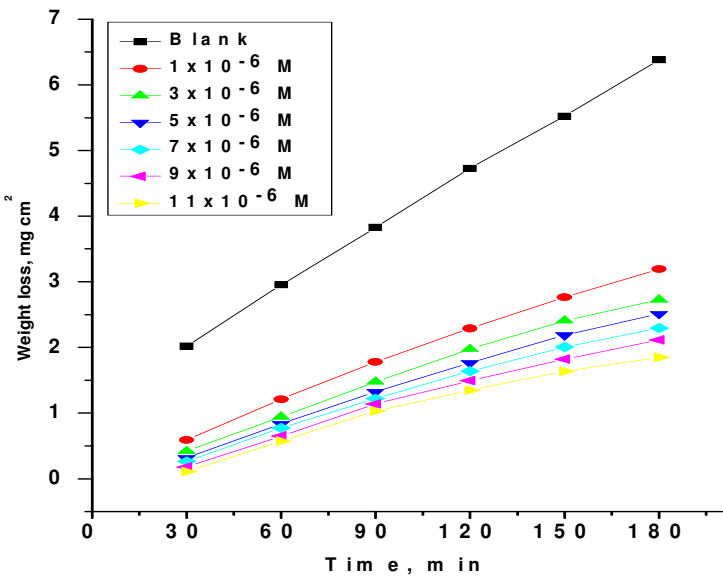


Figure 1: Weight-loss time curves for the dissolution of copper in the absence and presence of different concentrations of compound (I) at 30 ± 0.1 °C.

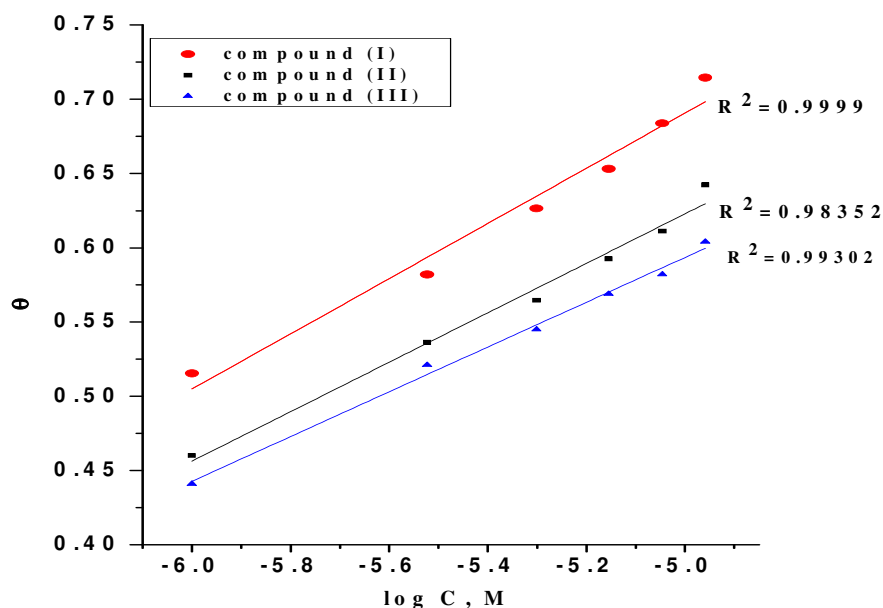


Figure 2: Curve fitting of corrosion data for copper in 2 M HNO₃ in presence of different concentrations of inhibitors to the Temkin isotherm at 30 ± 0.1 °C.

Table 4: Inhibitor binding constant (K_{ads}), free energy of binding (ΔG_{ads}) and later interaction parameter (a) for inhibitors at 30 °C.

Inhibitors	Temkin		
	a	K_{ads}	$-\Delta G_{ads}, \text{kJmol}^{-1}$
Compound (I)	60.76	1.19	10.56
Compound (II)	69.15	1.18	10.54
Compound (III)	78.86	1.16	10.50

3.3. Effect of Temperature

The effect of temperature on the inhibited acid-metal reaction is highly complex, because many changes occur on the metal surface, such as rapid etching and desorption of the inhibitor and the inhibitor itself, in some cases, may undergo decomposition and/or rearrangement. Generally the corrosion rate increases with the rise of temperature. It was found that the inhibition efficiency decreases with increasing temperature and increases with increasing the concentration of the inhibitor. The activation energy (E_a^*) of the corrosion process was calculated using Arrhenius equation [36]:

$$\text{C.R.} = A \exp(-E_a^* / RT) \quad (6)$$

where C.R. corrosion rate, A is Arrhenius constant, R is the gas constant and T is the absolute temperature. The values of activation energies E_a^* can be obtained from the slope of the straight lines of plotting log C.R. vs. $1/T$ in the presence and absence of investigated compounds at various temperatures Figure (3) and are given in Table (5), it is noted that the values of activation energy increase in the presence of inhibitors and with increase of the concentration of the inhibitors. This is due to the presence of a film of inhibitors on copper surface. The activation energy for the corrosion of copper in 2 M HNO₃ was found to be 21.06 kJ mol⁻¹ which is in good agreement with the work carried out by Fouda et al. [37] and others [38,39] An alternative formulation of the Arrhenius equation is the transition state equation [40]:

$$\text{C.R.} = RT/Nh \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \quad (7)$$

where h is Planck's constant, N is Avogadro's number, ΔS^* is the entropy of activation and ΔH^* is the enthalpy of activation. Figure (4) shows a plot of log (C.R. / T) vs. $(1/T)$. Straight lines are obtained with a slope of $(\Delta H^*/2.303 R)$ and an intercept of $(\log R/Nh + \Delta S^*/2.303 R)$ from which the values of ΔH^* and ΔS^* are calculated and also listed in Table (5). From inspection of Table (5) it is clear that the positive values of ΔH^* reflect that

the process of adsorption of the inhibitors on the copper surface is an endothermic process; it is attributable unequivocally to chemisorption [41]. Typically, the enthalpy of a chemisorption process approaches 100 kJ mol^{-1} . More interesting behavior was observed in Table (5) that positive ΔS^* values is accompanied with endothermic adsorption process. This agrees with what expected, when the adsorption is an endothermic process, it must be accompanied by an increase in the entropy energy change and vice versa [42].

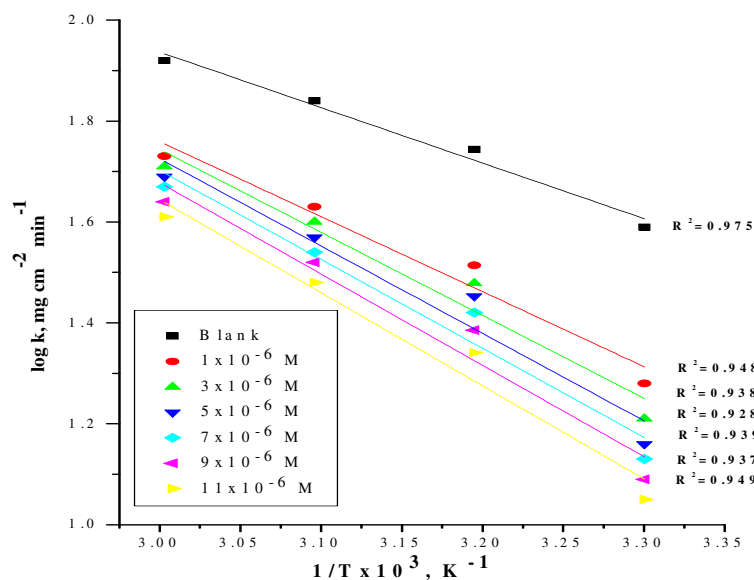


Figure 3: $\log k$ (corrosion rate) - $1/T$ curves for copper dissolution in 2 M HNO_3 in absent and present of different concentration of inhibitor (I).

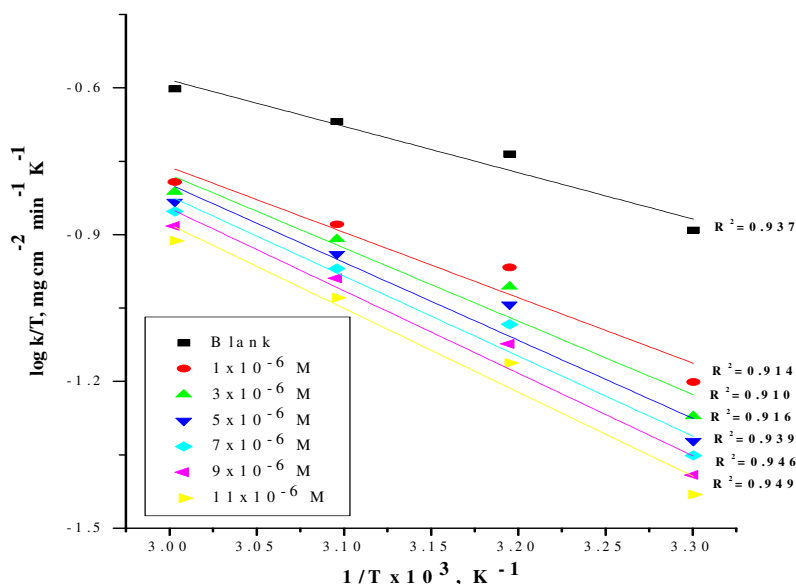


Figure 4: $\log (k \text{ corrosion rate}/T)$ - $1/T$ curves for copper dissolution in 2 M HNO_3 in absent and present of different concentration of inhibitor (I).

It is seen that investigated derivatives have inhibiting properties at all the studied temperatures and the values of % IE decrease with temperature increase. This shows that the inhibitor has experienced a significant decrease in

its protective properties with increase in temperature. This decrease in the protective properties of the inhibitor with increase in temperature may be connected with two effects; a certain drawing of the adsorption-desorption equilibrium towards desorption (meaning that the strength of adsorption process decreases at higher temperatures) and roughening of the metal surface which results from enhanced corrosion. These results suggest that physical adsorption may be the type of adsorption of the inhibitor on the copper surface.

Table 5: Activation parameters for the dissolution of copper in the presence and absence of different concentrations of inhibitors in 2M HNO₃.

Inhibitors	Conc. (M)	E_a^* kJ mol ⁻¹	ΔH^* kJ mol ⁻¹	$-\Delta S^*$ J mol ⁻¹ K ⁻¹
Blank	-----	21.06	18.12	154.42
Compound (I)	1x10 ⁻⁶	28.47	25.56	135.48
	3x10 ⁻⁶	31.50	28.65	126.48
	5 x10 ⁻⁶	33.16	30.51	121.32
	7x10 ⁻⁶	33.77	31.28	119.40
	9x10 ⁻⁶	34.66	32.25	117.11
	11x10 ⁻⁶	35.31	32.81	115.96
Compound (II)	1x10 ⁻⁶	26.35	23.62	141.22
	3x10 ⁻⁶	28.70	25.99	134.33
	5 x10 ⁻⁶	29.60	27.10	131.27
	7x10 ⁻⁶	29.67	27.12	131.14
	9x10 ⁻⁶	29.72	27.17	130.72
	11x10 ⁻⁶	30.20	27.73	130.27
Compound (III)	1x10 ⁻⁶	25.45	23.56	141.41
	3x10 ⁻⁶	28.32	26.30	133.95
	5 x10 ⁻⁶	28.43	26.32	133.33
	7x10 ⁻⁶	28.89	27.04	132.03
	9x10 ⁻⁶	28.99	27.84	131.99
	11x10 ⁻⁶	29.08	28.20	130.48

3.4. Potentiodynamic polarization measurements

Theoretically, copper can hardly be corroded in the deoxygenated acid solutions, as copper cannot displace hydrogen from acid solutions according to the theories of chemical thermodynamics [43-45]. However, this situation will change in nitric acid. Dissolved oxygen may be reduced on copper surface and this will allow

corrosion to occur. It is a good approximation to ignore the hydrogen evolution reaction and only consider oxygen reduction in the nitric acid solutions at potentials near the corrosion potentials [46].

Polarization measurements were carried out in order to gain knowledge concerning the kinetics of the cathodic and anodic reactions. Figure (5) shows the polarization behavior of copper electrode in 2 M HNO₃ in the absence and presence of various concentrations of compound (I). Figure (5) shows that both the anodic and cathodic reactions are affected by the addition of investigated organic derivatives and the inhibition efficiency increases as the inhibitor concentration increases, but the cathodic reaction is more inhibited, meaning that the addition of organic derivatives reduces the anodic dissolution of copper and also retards the cathodic reactions. Therefore, investigated organic derivatives are considered as mixed type inhibitors.

The values of electrochemical parameters such as corrosion current densities (i_{corr}), corrosion potential (E_{corr}), the cathodic Tafel slope (β_c), anodic Tafel slope (β_a) and inhibition efficiency (% IE) were calculated from the curves of Figure (5) and are listed in Table (6). The results in Table (6) revealed that the corrosion current density decreases obviously after the addition of inhibitors in 2 M HNO₃ and % IE increases with increasing the inhibitor concentration. In the presence of inhibitors E_{corr} was enhanced with no definite trend, indicating that these compounds act as mixed-type inhibitors in 2 M HNO₃. The inhibition efficiency was calculated using equation:

$$\% \text{IE}_p = [(i_{\text{corr}}^0 - i_{\text{corr}}) / i_{\text{corr}}^0] \times 100 \quad (8)$$

where i_{corr}^0 and i_{corr} are the uninhibited and inhibited corrosion current densities, respectively.

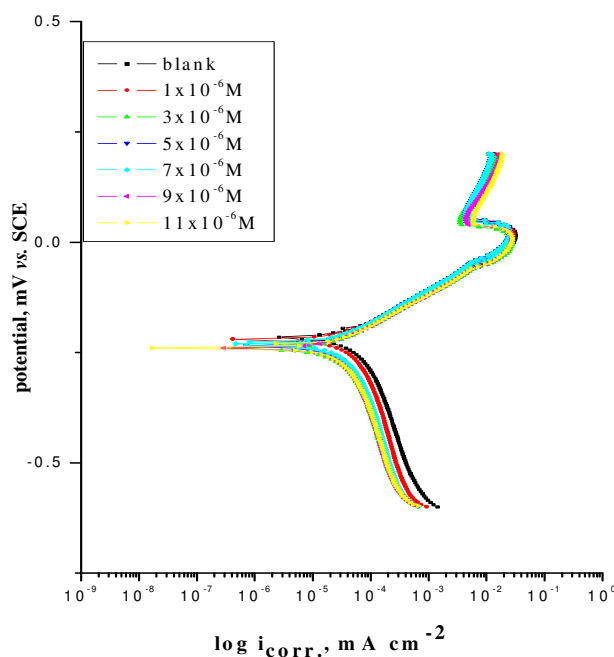


Figure 5: Potentiodynamic polarization curves for the corrosion of copper in 2 M HNO₃ in the absence and presence of various concentrations of compound (I) at 30 ± 0.1 °C.

Also it is obvious from Table (6) that the slopes of the anodic (β_a) and cathodic (β_c) Tafel lines remain almost unchanged upon addition of organic derivatives, giving rise to a nearly parallel set of anodic lines, and almost parallel cathodic plots results too. Thus the adsorbed inhibitors act by simple blocking of the active sites for both anodic and cathodic processes. In other words, the adsorbed inhibitors decrease the surface area for corrosion without affecting the corrosion mechanism of copper in 2 M HNO₃ solution, and only causes inactivation of a part of the surface with respect to the corrosive medium [47,48]. The inhibition efficiency of these compounds follows the sequence: compound (I) > compound (II) > compound (III). This sequence may attribute to free electron pair in nitrogen atom, π electrons on aromatic nuclei and the substituent in the

molecular structure of the inhibitor, and again reflects, as confirmed from weight loss measurements, the increased ability of compound (I) to inhibit nitric acid corrosion of copper as compared to compound (III). This is clearly seen from the highest efficiency recorded for compound (I).

Table 6: Effect of concentrations of the investigated compounds (I-III) on the free corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (β_a & β_c), degree of surface coverage (θ) and inhibition efficiency (% IE) for Copper in 2 M HNO_3 at 30 ± 0.1 °C.

Concentration, M.		$i_{\text{corr}} \times 10^{-6}$ mA cm^{-2}	$-E_{\text{corr}}$ mV vs (SCE)	$\beta_a \times 10^{-3}$, mV dec^{-1}	$\beta_c \times 10^{-3}$, mV dec^{-1}	θ	% IE
2 M HNO_3		69.1	216	119.6	341.6	-	-
Compound (I)	1×10^{-6}	18.3	220	43.5	83.2	0.735	73.5
	3×10^{-6}	18.1	240	60.2	142.6	0.738	73.8
	5×10^{-6}	17.8	236	65.8	104.2	0.742	74.2
	7×10^{-6}	17.2	230	77.1	211.4	0.751	75.1
	9×10^{-6}	16.8	240	50.9	102.4	0.756	75.6
	11×10^{-6}	13.8	240	69.3	160.0	0.800	80.0
Compound (II)	1×10^{-6}	25.3	231	76.3	256.5	0.633	63.3
	3×10^{-6}	25.2	231	66.8	135.0	0.635	63.5
	5×10^{-6}	25.1	230	77.0	242.0	0.636	63.6
	7×10^{-6}	23.1	235	64.6	160.8	0.665	66.5
	9×10^{-6}	21.0	241	66.9	181.0	0.696	69.6
	11×10^{-6}	18.5	226	53.5	100.8	0.732	73.2
Compound (III)	1×10^{-6}	43.1	235	103.8	331.2	0.376	37.6
	3×10^{-6}	33.3	235	89.7	237.0	0.518	51.8
	5×10^{-6}	28.5	236	76.4	197.1	0.587	58.7
	7×10^{-6}	28.2	218	62.2	162.4	0.591	59.1
	9×10^{-6}	27.0	235	72.0	192.0	0.609	60.9
	11×10^{-6}	26.3	217	55.8	108.6	0.619	61.9

3.5 Electrochemical impedance spectroscopy (EIS)

EIS is well-established and powerful technique in the study of corrosion. Surface properties, electrode kinetics and mechanistic information can be obtained from impedance diagrams [49-53]. Figure (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 compounds at 30 ± 0.1 °C. The increase in the size of the capacitive loop with the addition of organic derivatives shows that a barrier gradually forms on the copper surface. The increase in the capacitive loop size (Figure (6a)) enhances, at a fixed inhibitor concentration, following the order: compound (I) > compound (II) > compound (III), confirming the highest inhibitive influence of compound (I). Bode plots (Figure (6b)), shows that the total impedance increases with increasing inhibitor concentration ($\log Z$ vs. $\log f$). But ($\log f$ vs. phase), also Bode plot shows the continuous increase in the phase angle shift, obviously

correlating with the increase of inhibitor adsorbed on copper surface. The Nyquist plots do not yield perfect semicircles as expected from the theory of EIS. The deviation from ideal semicircle was generally attributed to the frequency dispersion [54] as well as to the inhomogeneities of the surface. EIS spectra of the organic additives were analyzed using the equivalent circuit, Figure (7), which represents a single charge transfer reaction and fits well with our experimental results.

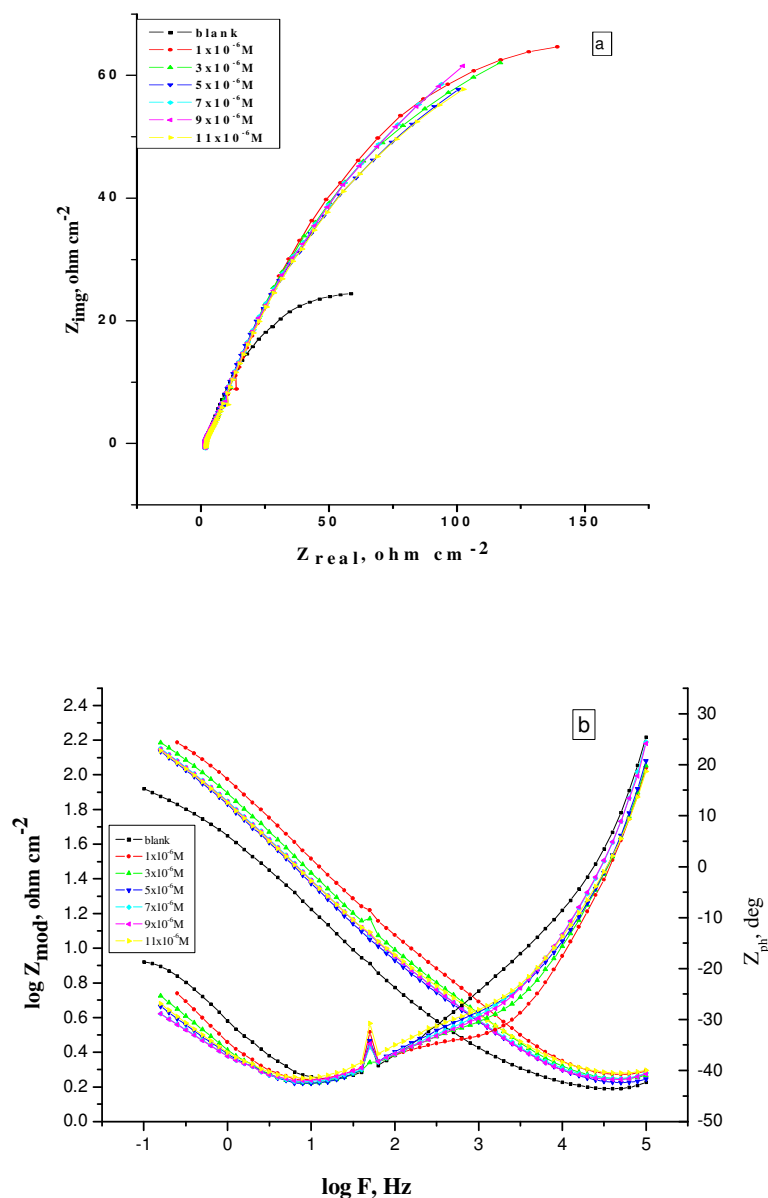


Figure 6: The Nyquist (a) and Bode (b) plots for corrosion of Copper in 2 M HNO₃ in absence and presence of different concentrations of compound (I) at 30 ± 0.1 °C.

The constant phase element, CPE, is introduced in the circuit instead of a pure double layer capacitor to give a more accurate fit [55]. The double layer capacitance, C_{dl} , for a circuit including a

$$C_{dl} = Y_0 \omega^{n-1} / \sin [n (\pi/2)] \quad (9)$$

where Y_0 is the magnitude of the CPE, $\omega = 2\pi f_{max}$, f_{max} is the frequency at which the imaginary component of the impedance is maximal and the factor n is an adjustable parameter that usually lies between 0.50 and 1.0. After analyzing the shape of the Nyquist plots, it is concluded that the curves approximated by a single capacitive semicircles, showing that the corrosion process was mainly charged-transfer controlled [56-58]. The general shape of the curves is very similar for all samples (in presence or absence of inhibitors at different

immersion times) indicating that no change in the corrosion mechanism [59]. From the impedance data (Table (7)), we conclude that the value of R_{ct} increases with increasing the concentration of the inhibitors and this indicates an increase in % IE, which in concord with the weight loss results obtained.

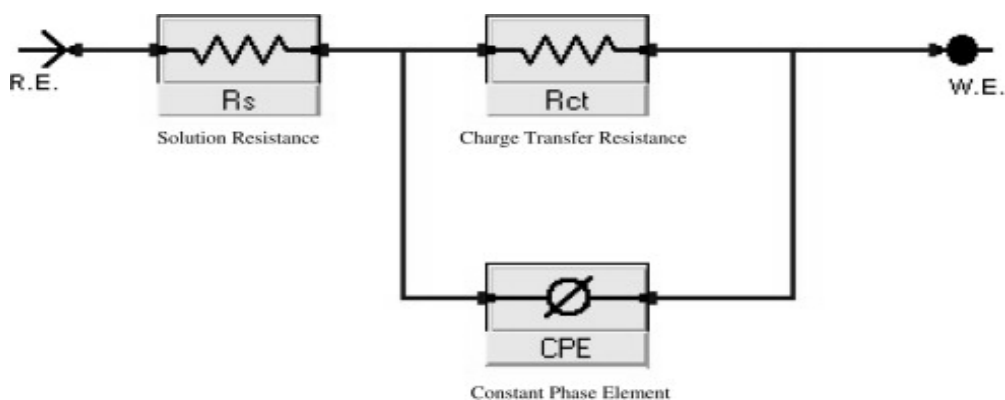


Figure 7: Equivalent circuit model used to fit experimental EIS.

Table 7: Electrochemical kinetic parameters obtained by EIS technique for Copper in 2 M HNO_3 without and with various concentrations of compounds (I-III) at 30 ± 0.1 °C.

Inhibitors	Conc., M	$R_s, \Omega \text{cm}^2$	$Y_{os}, \times 10^{-3} \mu\Omega^{-1} \text{s}^n$	$n \times 10^{-3}$	$R_{ct}, \Omega \text{cm}^2$	$C_{dl} \times 10^{-4}, \mu\text{Fcm}^{-2}$	θ	% IE
Compound (I)	Blank	1.452	5.737	553.8	108.7	7.08	-----	----
	1×10^{-6}	1.533	4.109	516.1	320.0	2.33	0.660	66.0
	3×10^{-6}	1.485	4.966	511.2	322.2	2.19	0.662	66.2
	5×10^{-6}	1.548	4.713	514.5	324.1	2.07	0.664	66.4
	7×10^{-6}	1.557	3.304	517.4	325.4	2.02	0.665	66.5
	9×10^{-6}	1.514	4.487	513.8	328.0	1.74	0.668	66.8
	11×10^{-6}	1.670	4.966	502.7	330.3	1.55	0.670	67.0
Compound (II)	1×10^{-6}	1.158	4.468	516.9	282.0	2.80	0.614	61.4
	3×10^{-6}	1.274	3.154	531.7	296.9	2.78	0.633	63.3
	5×10^{-6}	1.546	2.669	522.0	300.1	2.77	0.637	63.7
	7×10^{-6}	1.687	2.483	515.5	305.8	2.66	0.644	64.4
	9×10^{-6}	1.241	4.375	519.6	308.5	2.52	0.647	64.7
	11×10^{-6}	1.267	3.678	522.6	315.2	2.35	0.655	65.5
Compound (III)	1×10^{-6}	1.683	3.667	545.5	143.7	3.83	0.243	24.3
	3×10^{-6}	1.517	3.977	536.7	169.6	3.68	0.359	35.9
	5×10^{-6}	1.184	5.213	516.7	250.6	3.62	0.566	56.6
	7×10^{-6}	1.589	3.276	525.8	262.6	2.96	0.585	58.5
	9×10^{-6}	1.570	3.259	510.5	277.9	2.92	0.608	60.8
	11×10^{-6}	1.479	4.061	516.6	280.4	2.83	0.612	61.2

In fact the presence of inhibitors enhances the value of R_{ct} in acidic solution. Values of double layer capacitance are also brought down to the maximum extent in the presence of inhibitor and the decrease in the values of CPE follows the order similar to that obtained for i_{corr} in this study. The decrease in CPE/C_{dl} results from a decrease in local dielectric constant and/or an increase in the thickness of the double layer, suggesting that organic derivatives inhibit the copper corrosion by adsorption at metal/acid [60,61]. The inhibition efficiency was calculated from the charge transfer resistance data from equation (10) [62]:

$$\% IE_{EIS} = [1 - (R_{ct}^0 / R_{ct})] \times 100 \quad (10)$$

where R_{ct}^0 and R_{ct} are the charge-transfer resistance values without and with inhibitor respectively.

3.6. Electrochemical Frequency Modulation Technique (EFM)

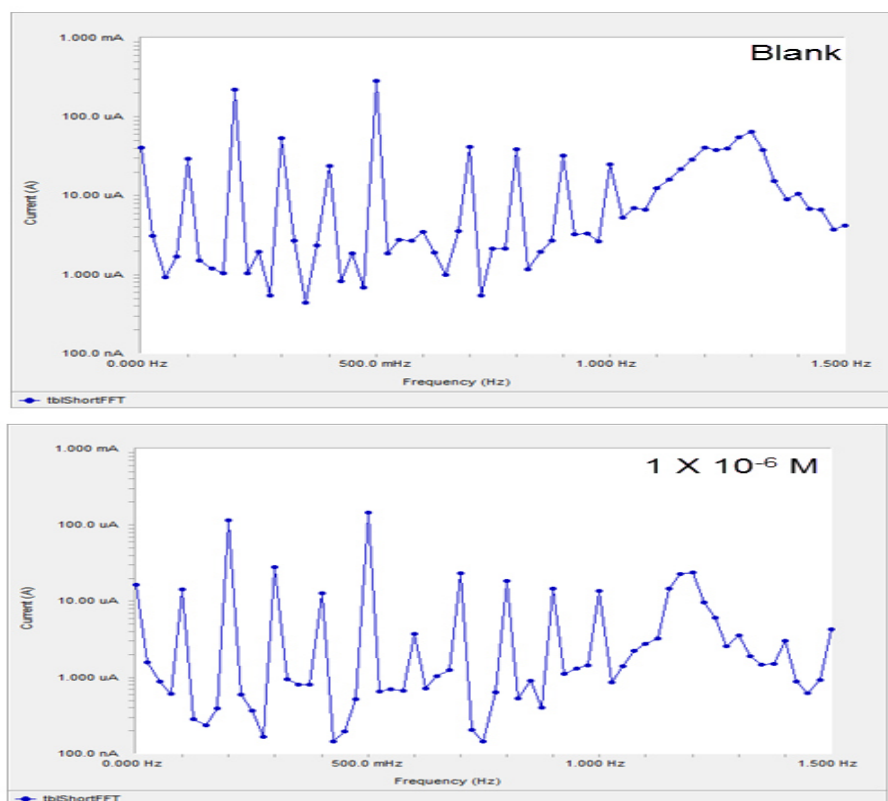
EFM is a nondestructive corrosion measurement technique that can directly and quickly determine the corrosion current values without prior knowledge of Tafel slopes, and with only a small polarizing signal. These advantages of EFM technique make it an ideal candidate for online corrosion monitoring [63]. The great strength of the EFM is the causality factors which serve as an internal check on the validity of EFM measurement. The causality factors CF-2 and CF-3 are calculated from the frequency spectrum of the current responses.

Figure (8) shows the EFM Intermodulation spectrums of copper in nitric acid solution containing different concentrations of compound (I). Similar curves were obtained for other compounds (not shown). The harmonic and intermodulation peaks are clearly visible and are much larger than the background noise. The two large peaks, with amplitude of about 200 μA , are the response to the 40 and 100 mHz (2 and 5 Hz) excitation frequencies. It is important to note that between the peaks there is nearly no current response (<100 nA). The experimental EFM data were treated using two different models: complete diffusion control of the cathodic reaction and the “activation” model. For the latter, a set of three non-linear equations had been solved, assuming that the corrosion potential does not change due to the polarization of the working electrode [64]. The larger peaks were used to calculate the corrosion current density (i_{corr}), the Tafel slopes (β_c and β_a) and the causality factors (CF-2 and CF-3). These electrochemical parameters were listed in Table (8). The data presented in Table (8) obviously show that, the addition of any one of tested compounds at a given concentration to the acidic solution decreases the corrosion current density, indicating that these compounds inhibit the corrosion of copper in 2 M HNO_3 through adsorption. The causality factors obtained under different experimental conditions are approximately equal to the theoretical values (2 and 3) indicating that the measured data are verified and of good quality. The inhibition efficiencies% IE_{EFM} increase by increasing the inhibitor concentrations and was calculated as from equation (11):

$$\% \text{IE}_{\text{EFM}} = [1 - (i_{\text{corr}} / i_{\text{corr}}^0)] \times 100 \quad (11)$$

where i_{corr}^0 and i_{corr} are corrosion current densities in the absence and presence of inhibitor, respectively.

The inhibition sufficiency obtained from this method is in the order: compound (I) > compound (II) > compound (III).



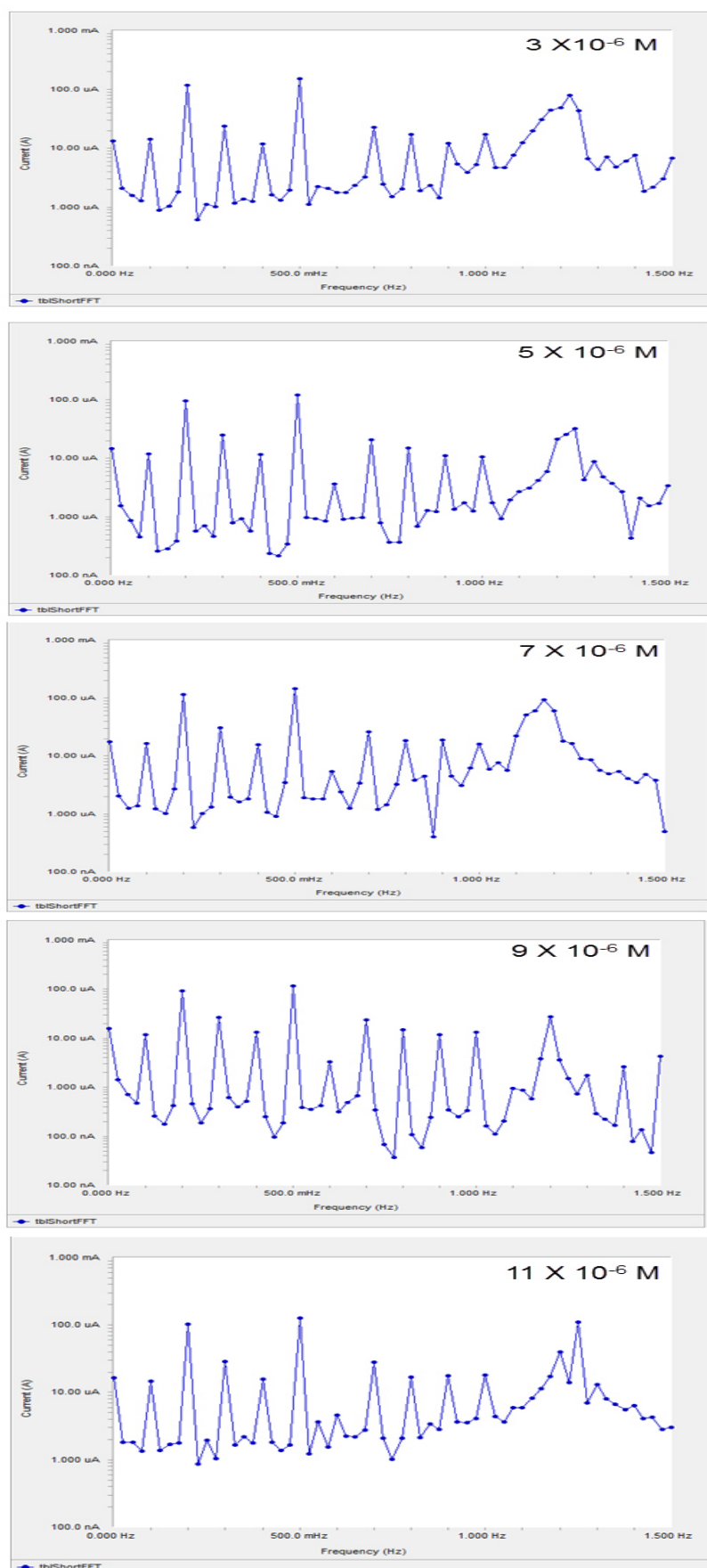


Figure 8: EFM spectra for copper in 2 M HNO₃ in the absence and presence of different concentrations of compound (I) at 30 ± 0.1 °C.

Table 8: Electrochemical kinetic parameters obtained by EFM technique for copper in 2 M HNO₃ without and with various concentrations of compounds (I-III) at 30 °C.

Inhibitors	Conc., M. M	$i_{corr.},$ $\mu A\ cm^2$	$\beta_a \times 10^{-3},$ $mV\ dec^{-1}$	$\beta_c \times 10^{-3},$ $mV\ dec^{-1}$	CF-2	CF-3	θ	%IE
Compound (I)	Blank	127.2	27.40	39.91	1.95	2.77	-	-
	1×10^{-6}	65.63	27.36	41.14	2.10	3.36	0.483	48.3
	3×10^{-6}	59.84	24.92	33.77	1.50	3.30	0.529	52.9
	5×10^{-6}	55.23	27.32	42.35	1.85	2.93	0.565	56.5
	7×10^{-6}	51.73	21.95	31.18	1.74	3.13	0.592	59.2
	9×10^{-6}	49.87	25.23	40.51	1.80	3.14	0.607	60.7
	11×10^{-6}	49.59	23.08	35.53	1.85	3.12	0.609	60.9
Compound (II)	1×10^{-6}	84.21	29.49	41.69	1.49	3.15	0.337	33.7
	3×10^{-6}	82.46	22.86	36.91	2.10	2.88	0.351	35.1
	5×10^{-6}	79.15	29.01	40.15	1.75	2.88	0.377	37.7
	7×10^{-6}	78.90	27.36	37.24	1.77	3.04	0.379	37.9
	9×10^{-6}	77.65	28.94	41.75	1.99	2.83	0.389	38.9
	11×10^{-6}	69.22	26.82	37.62	1.92	2.87	0.455	45.5
Compound (III)	1×10^{-6}	122.5	29.50	43.41	1.82	2.95	0.036	3.6
	3×10^{-6}	118.4	24.77	36.65	1.99	3.05	0.068	6.8
	5×10^{-6}	99.19	29.89	42.43	1.72	3.09	0.219	21.9
	7×10^{-6}	93.96	35.58	48.99	1.82	3.15	0.260	26.0
	9×10^{-6}	93.58	33.30	48.23	1.93	3.01	0.263	26.3
	11×10^{-6}	89.08	30.87	44.32	2.03	3.04	0.299	29.9

3.7. Quantum chemical calculations

Figure (9) represents the molecular orbital plots and Mulliken charges of investigated compounds. 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 lowest unoccupied molecular orbitals (LUMO) and energy of highest occupied molecular orbitals (HOMO) (E_{HOMO} and E_{LUMO}), the formation heat ΔH_f and energy gap ΔE , are calculated by semi-empirical AM1, MNDO and PM3 methods has been given in Table (9). It has been reported that the higher or less negative E_{HOMO} is associated of inhibitor, the greater the trend of offering electrons to unoccupied d orbital of the metal, and the higher the corrosion inhibition efficiency, in addition, the lower E_{LUMO} , the easier the acceptance of electrons from metal surface [65].

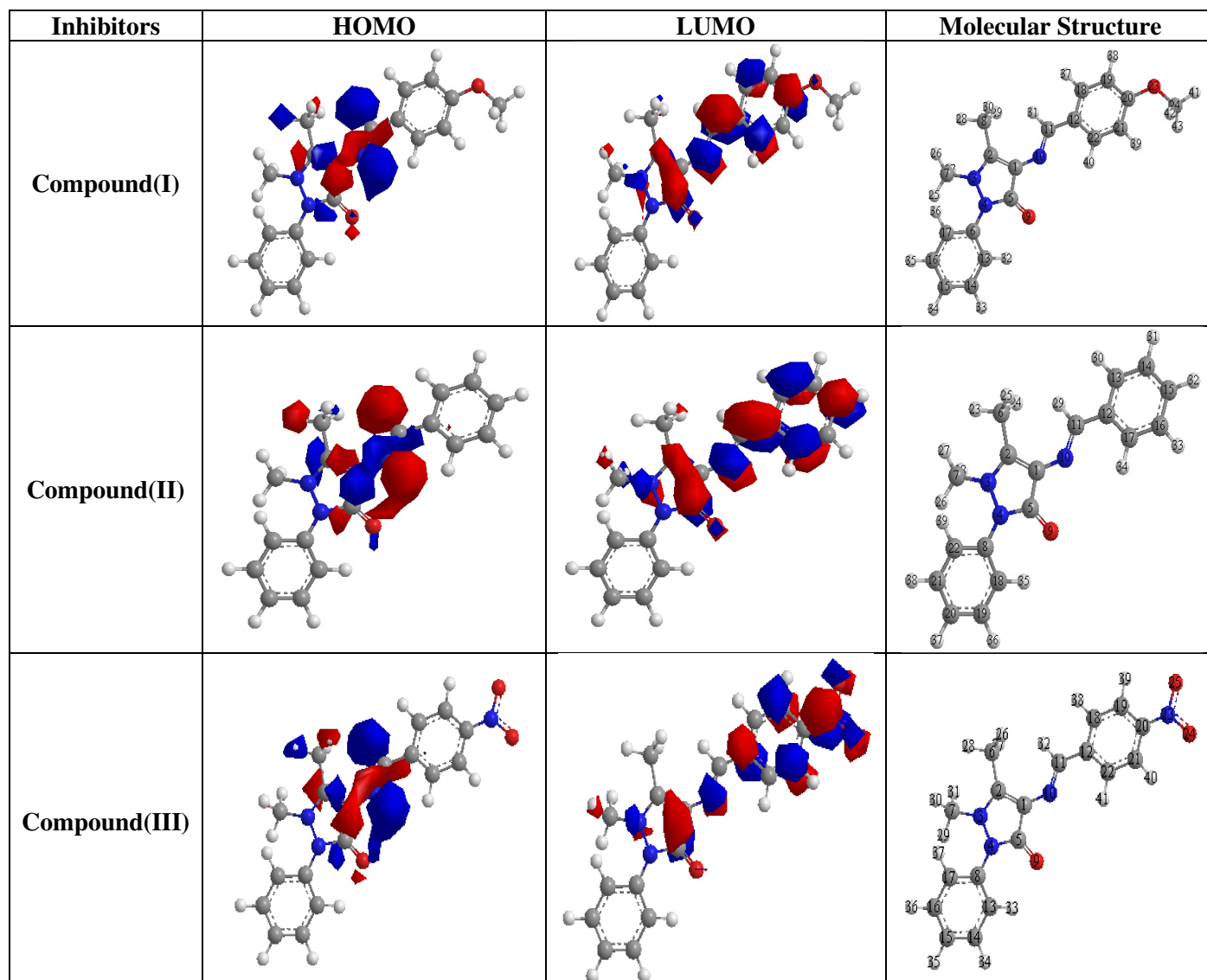


Figure 9: Molecular orbital plots of investigated compounds.

Table 9: The calculated quantum chemical properties for investigated compounds.

	Compound (I)	Compound (II)	Compound (III)
$-E_{\text{HOMO}}$ (a.u)	0.2648	0.2655	0.2684
$-E_{\text{LUMO}}$ (a.u)	0.1881	0.0701	0.0521
ΔE (a.u)	0.077	0.195	0.216
η (a.u)	0.1063	0.0976	0.0401
σ (a.u) ⁻¹	9.4073	10.2459	24.9376
$-\rho$ (a.u)	0.1584	0.1678	0.2282
χ (a.u)	0.1584	0.1678	0.2282
S (a.u) ⁻¹	4.7036	5.1229	12.4688
ω (a.u)	0.1180	0.1442	0.6493
ΔN_{max}	1.4901	1.7192	5.6907

From Table (9), it is clear that ΔE obtained by the four methods in case of compound (III) is lower than compound (I), which enhance the assumption that compound (I) molecule will absorb more strongly on copper surface than compound (III), due to facilitating of electron transfer between molecular orbital HOMO and

LUMO which takes place during its adsorption on the metal surface and thereafter presents the maximum of inhibition efficiency. Also it can be seen that E_{HOMO} increases from compound (I) to compound (III) facilitates the adsorption and the inhibition by supporting the transport process through the adsorbed layer. Reportedly, excellent corrosion inhibitors are usually those organic compounds who are not only offer electrons to unoccupied orbital of the metal, but also accept free electrons from the metal [66,67]. It can be seen that all calculated quantum chemical parameters validate these experimental results.

3.8. Inhibition mechanism

Inhibition of the corrosion of copper in 2 M HNO_3 solution by investigated compounds is determined by weight loss, potentiodynamic 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 adsorption of inhibitor depends on its concentration. As shown in Figure (10), at adsorption density less than a monolayer (Figure (10a)), most of the nucleation sites are still possibly exposed to HNO_3 , since inhibitor adsorbs less likely on them. When the adsorption density reaches monolayer adsorption (Figure (10b)), some of the nucleation sites begin to be covered by inhibitor molecules. At maximum adsorption density (Figure (10c)), the inhibitor molecules cover the whole surface, including the nucleation sites, and then complete inhibition occurs.

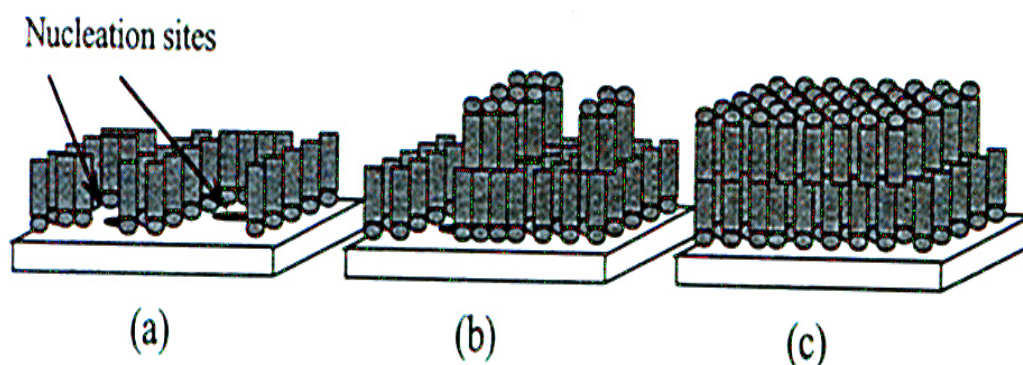


Figure 10: Adsorption schemes for organic additives as inhibitors at:
(a) low concentration, (b) intermediate concentration, (c) high concentration on copper
(b)

The corrosion inhibition is due to 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 copper surface is assumed to take place mainly through the active centers attached to the inhibitor and would depend on their charge density. Transfer of lone pairs of electrons on the nitrogen atoms to the copper surface to form a coordinate type of linkage is favored by the presence of a vacant orbital in copper 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, 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 (I) > compound (II) > compound (III).

Compound (I) exhibits excellent inhibition power due to: (i) the presence of $p\text{-OCH}_3$ group which is an electron donating group with negative Hammett constant ($\sigma = -0.27$), 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 (II) comes after compound (I) in inhibition efficiency. This is due to it has 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 (III) comes after compound (II) in inhibition efficiency. This is due to presence of $p\text{-NO}_2$ which has positive Hammett constant ($\sigma = +0.78$), i.e. group which lower the electron density on the molecule and hence, lower inhibition efficiency.

Conclusions

- All the investigated compounds are good corrosion inhibitors for copper in 2M HNO₃ solution. The effectiveness of these inhibitors depends on their structures. The variation in inhibitive efficiency depends on the type and the nature of the substituent present in the inhibitor molecule
- EFM can be used as a rapid and nondestructive technique for corrosion measurements without prior knowledge of Tafel slopes
- The results of EIS revealed that an increase in the charge transfer resistance and a decrease in double layer capacitances when the inhibitor is added and hence an increase in % IE. This is attributed to increase of the thickness of the electrical double layer
- The adsorption of the inhibitors are adsorbed on copper surface obeys the Temkin adsorption isotherm model
- The results obtained from chemical and electrochemical measurements were in good agreement. The order of % IE of these investigated compounds is in the following order: compound (I) > compound (II) > compound (III)
- The values of E_{HOMO} and E_{LUMO} decreases in an order runs parallel to the increase in % IE obtained which support the previous order

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