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RESEARCH ARTICLE

New Aryl azo- thiazolin 4 -one derivatives as inhibitors for the acid corrosion of α -brass

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Manuscript Info	Abstract
<i>Manuscript History:</i> Received 13 May 2014 Final Accepted: 18 June 2014 Published Online: July 2014	The effect of the addition of some aryl azo- thiazolin 4-one derivatives on the corrosion of α -brass in nitric acid investigated using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) measurements. It was found that the investigated compounds behave as inhibitors. The inhibition
<i>Key words:</i> Moringa; 3.5 % NaCl and 16 ppm Solution; Zinc Corrosion, Weight Loss; Potentiodynamic Polarization; EIS; EFM	efficiency increases with increasing the inhibitor concentration, but decreases with increasing the temperature. The adsorption of these compounds on the α -brass surface follows Temkin's adsorption isotherm. The effect of the temperature on the corrosion of α -brass in 1 M nitric acid was studied. Potentiodynamic polarization studies showed that these compounds are
*Corresponding Author	mixed-type inhibitors and the results obtained from the techniques are in good agreement.
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Introduction

Copper and its alloys, because of their excellent resistance to corrosion in neutral aggressive media and their ease of processing, they are widely used in industries, particularly as condensers and heat exchangers in power plants [1]. Electrochemical techniques are powerful tools to study brass since they offer valuable information about the phase and chemical composition [2]. Such techniques have also proved to be useful to study the evolution of brass in the environment [3] to understand the degeneration process and to prevent oxidation of the alloy [4-6]. A number of studies have recently appeared in the literature [7-9] on the topic of the corrosion inhibition of α -brass in acidic medium. The inhibition efficiency of organic compounds is strongly dependent on the structure and chemical properties of the layer formed on conditions. Heterocyclic compounds are well known for their efficiencies as corrosion inhibitors and those containing nitrogen have been frequently referred to in the literature [10-15]. The investigated compounds offer interesting possibilities for corrosion inhibition and are of particular interest

because of their high molecular size and their molecules contain electronegative atoms such as nitrogen, oxygen and sulphur, such these compounds should be good corrosion inhibitors.

The aim of this paper is to describe an investigation of the inhibition of corrosion of α -brass in 1 M HNO₃ solutions by some arylazothiazolin derivatives using chemical and electrochemical measurements.

Experimental technique Materials

The experiments were performed with local commercial α -brass (Helwan Company of Non-Ferrous Industries, Egypt) with the following composition (weight %) Cu 60, Zn 40. The inhibitors used were selected from thiazolin derivatives with chemical structures shown in Table 1. The organic compounds were prepared, purified and identified according to the recommended method [16].

Solutions

The aggressive solutions, 1 M HNO₃ were prepared by dilution of analytical grade (70 %) HNO₃ acid by bidistilled water. All chemicals and reagents were of analytical grade. The measurements were performed in 1 M HNO₃ without and with the presence of the investigated compounds in the concentration range ($1x10^{-6}$ to $11x10^{-6}$ M). Arylazothiazolin derivatives were prepared as reported before [16]. Table 1 shows the structures, names, molecular weights and molecular formulas of these compounds.

Weight loss tests

Seven parallel α -brass sheets of 2 × 2 × 0.2 cm were abraded with emery paper (grade 320–500–800-1200) and then washed with bidistilled water and acetone. After accurate weighing, the specimens were immersed in a 100 ml beaker, which contained 100 ml of HNO₃ with and without addition of different concentrations of the investigated compounds. All the aggressive acid solutions were open to air. After 3 h, the specimens were taken out, washed, dried, and weighed accurately. The average weight loss of the seven parallel α -brass sheets could be obtained. The inhibition efficiency (%IE) and the degree of surface coverage, θ , of investigated compounds for the corrosion of α -brass in HNO₃ were calculated from Eq. (1) [17]:

% IE = $\theta \times 100 = [1 - (W / W^{\circ})] \times 100$

(1)

Where W° and W are the values of the average weight loss without and with addition of the inhibitor, respectively

Electrochemical measurements

Potentiodynamic polarization measurements

Polarization experiments were carried out in a conventional three-electrode cell with platinum gauze as the auxiliary electrode 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 α -brass sheet of equal composition embedded in 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 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. Then i_{corr} was used for the calculation of inhibition efficiency and surface coverage (θ) as below:

% IE= $\theta \times 100 = [1 - (i_{corr}/i_{corr}^{\circ})] \times 100$

(2)

where i°_{corr} and i_{corr} are corrosion current densities in the absence and presence of inhibitor, respectively.

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 version 6.03.

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 [18-20]. 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 [21].

The electrode potential was allowed to stabilize for 30 min before starting the measurements. All the experiments were conducted at $25 \pm 1^{\circ}$ C. Measurements were performed using Gamry Instrument Potentiostat/ Galvanostat/ZRA (PCI4-G750). This includes a Gamry framework system v 6.03 Gamry applications include DC 105 software for DC corrosion measurements, EIS 300 software for electrochemical impedance spectroscopy measurements and EFM 140 for electrochemical frequency modulation measurements along with a computer for collecting data. Echem analyst version 6.03 software was used for plotting, graphing, and fitting data.

Quantum calculation

All the quantum chemical study has been carried out using semi-empirical method (PM3), available by Material studio version 6. Molecular orbital calculation was based on semi-empirical method. This method has been used with full geometry optimization.

Surface examination

The surface films were formed on the α -brass specimens by immersing them in inhibitor solutions for a period of 24 h. After the immersion period, the specimens were taken out, dried and the nature of the film formed on the surface of the metal specimen was analyzed by EDX and SEM techniques. Examination of α -brass surface after 24 h exposure to the 1 M HNO₃ solution without and with inhibitor was carried out by JOEL JSM-6510LV Scanning Electron Microscope. Rough elemental analyses for the exposed surface were conducted by EDX technique.

1 ai	sie 1. Chemical structures, names, molec	ular weights and molecular formulas (
Inhibitor	Structures	Names	Mol. Weights, Mol. Formulas
Α		(Z)-2-cyano-2-((Z)-4-(2-(4- hydroxyphenyl)hydrazono)-5-oxo-3- phenylthiazolidin-2- ylidene)acetichypochlorous anhydride	414.82 C ₁₈ H ₁₁ N ₄ O ₄ SCl
В	H ₃ C	(Z)-2-cyano-2-((Z)-4-(2-(4- hydroxyphenyl)hydrazono)-5-oxo-3- phenylthiazolidin-2-ylidene)acetic hypochlorous anhydride	412.85 C ₁₉ H ₁₃ N ₄ O ₃ SCl
С	Br NC COOCI	(Z)-2-((Z)-4-(2-(4- bromophenyl)hydrazono)-5-oxo-3- phenylthiazolidin-2-ylidene)-2- cyanoacetic hypochlorous anhydride	477.72 C ₁₈ H ₁₀ N ₄ O ₃ SClBr

Table 1: Chemical structures, names, molecular weights and molecular formulas of inhibitors

Results and Discussion

Weight-loss measurements

Weight-loss of α -brass was determined, at various time intervals, in the absence and presence of different concentrations of thiazolin derivatives compounds. The obtained weight-loss time curves are represented in Figure 1 for inhibitor (A), the most effective one. Similar curves were obtained for other inhibitors (not shown). The inhibition efficiency of corrosion was found to be dependent on the inhibitor concentration. The curves obtained in the presence of inhibitors fall significantly below that of free acid. In all cases, the increase in the inhibitor concentration was accompanied by a decrease in weight-loss and an increase in the percentage inhibitors for α -brass dissolution in nitric acid solution. Also, the degree of surface coverage (Θ) calculated from Eq. (1), would increase by increasing the inhibitor concentration. In order to get a comparative view, the variation of the percentage inhibition (% IE) of the three inhibitors with their molar concentrations was calculated according to Eq. (1). The values obtained are summarized in Table 2. Careful inspection of these results showed that, at the same inhibitor concentration, the order of inhibition efficiency is as follows: A > B > C



Figure 1: Weight loss-time curves for the corrosion of α-brass in 1 M HNO₃ in the absence and presence of different concentrations of inhibitor (A) at 25 °C

Table 2: Values of inhibition efficiencies (% IE) and surface coverage (θ) of inhibitors for the corrosion of θ	a-10
brass in 1 M HNO ₃ from weight-loss measurements at different concentrations and at 25°C	

[inh] X10 ⁶ M	Α		F	}	С	
	θ	% IE	θ	% IE	θ	% IE
1	0.531	53.1	0.417	41.7	0.343	34.3
3	0.623	62.3	0.525	52.5	0.474	47.4
5	0.696	69.6	0.606	60.6	0.513	51.3
7	0.782	78.2	0.703	70.3	0.578	57.8
9	0.829	82.9	0.827	82.7	0.699	69.9
11	0.913	91.3	0.878	87.8	0.812	81.2

Effect of Temperature

The effect of temperature on the corrosion rate of α -brass in absence and presence of different concentrations of investigated compounds was studied in the temperature range of **25-45°C** using weight loss measurements. As shown from Table 3, when the temperature increases the rate of corrosion increases and the inhibition efficiency decreases for compound (A) the most effective one. The adsorption behavior of inhibitors on α -brass surface occurs through physical adsorption.

Table 3: Inhibition efficiencies % IE and corrosion rate (C.R) of inhibitor (A) for the corrosion of α-brass in 1 M HNO₃ from weight-loss measurements at different concentrations at temperature range of 25-45°C

[inh] x10 ⁶ M	298	3 K	30.	3K	30	8K	313	K	31	8K
	C.R	% IE	C.R	%IE	C.R	%IE	C.R	%IE	C.R	%IE
1	0.26	53.1	0.42	48.4	0.43	36.7	0.73	31.0	0.91	26.7
3	0.21	62.3	0.33	55.8	0.34	47.2	0.63	43.7	0.76	42.4
5	0.18	69.6	0.25	60.6	0.28	57.1	0.56	55.7	0.62	51.2
7	0.13	78.2	0.18	72.9	0.24	69.7	0.38	68.9	0.44	65.1
9	0.08	82.9	0.13	80.9	0.20	78.4	0.24	77.6	0.27	73.7
11	0.03	91.3	0.07	91.2	0.12	89.7	0.16	87.7	0.15	82.1

Adsorption Isotherm

One of the most convenient ways of expressing adsorption quantitatively is by deriving the adsorption isotherm that characterizes the metal/inhibitor/ environment system. Various adsorption isotherms were applied to fit θ values, but the best fit was found to obey Temkin adsorption isotherm which are represented in Figure 2 for investigated compounds, Temkin adsorption isotherm may be expressed by: $a\Theta = \ln K_{ads} C$ (3)

where C is the concentration (mol L⁻¹) of the inhibitor in the bulk electrolyte, is the degree of surface coverage (Θ = % IE/100), K ads is the adsorption equilibrium constant. A plot of Θ versus log C should give straight lines with slope equal 2.303/a and the intercept is $(2.303/a \log K_{asd})$. In order to get a comparative view, the variation of the adsorption equilibrium constant (K_{ads}) of the inhibitors with their molar concentrations was calculated according to Eq. (2). The experimental data give good curves fitting for the applied adsorption isotherm as the correlation coefficients (R^2) were in the range (0.943- 0.999). The values obtained are given in Table 4.

These results confirm the assumption that, these compounds are adsorbed on the metal surface via the lone pair of electrons of (N, S, O) atoms. The extent of inhibition is directly related to the performance of adsorption layer which is a sensitive function of the molecular structure. The equilibrium constant of adsorption K_{ads} obtained from the intercepts of Temkin adsorption isotherm is related to the free energy of adsorption ΔG°_{ads} as follows: (4)

 $K_{ads} = 1/55.5 \exp \left[-\Delta G^{\circ}_{ads} / RT\right]$

where, 55.5 is the molar concentration of water in the solution in M^{-1}



Figure 2: Temkin's adsorption isotherm of investigated compounds on α-brass surface in 1 M HNO₃ at 25 °C

Temp	'emp A		В		С		
٥C	${{\rm K}_{\rm ads}~{\rm x10^{-3}}\over {\rm M}^{-1}}$	a	K _{ads} x10 ⁻³ M ⁻¹	a	$\begin{array}{c} K_{ads} \ x10^{-3} \\ M^{-1} \end{array}$	a	
25	1.34	8.2	1.37	7.2	1.45	4.6	
30	1.38	5.9	1.40	5.5	1.40	3.7	
35	1.41	4.7	1.45	4.0	1.46	4.4	
40	1.43	4.3	1.46	3.8	1.46	4.1	
45	1.44	4.0	1.44	3.8	1.47	5.8	

Table 4. Equilibrium constant (K_{ads}) of investigated compounds adsorbed on α -brass surface in 1M HNO₃ at 25°C

Plot of (ΔG^{o}_{ads}) versus T Figure 3 gave the heat of adsorption (ΔH^{o}_{ads}) and the standard entropy (ΔS^{o}_{ads}) according to the thermodynamic basic equation 5:

 $\Delta G^{o}_{ads} = \Delta H^{o}_{ads} - T \Delta s^{o}_{ads}$

(5)

Table 5 clearly shows a good dependence of ΔG°_{ads} on T, indicating the good correlation among thermodynamic parameters. The negative value of ΔG°_{ads} ensures the spontaneity of the adsorption process and stability of the adsorbed layer on the brass surface. Generally, values of ΔG°_{ads} around -20 kJ mol⁻¹ or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal (physical adsorption);those around -40 kJ mol⁻¹ or higher involves charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of bond (chemisorption) [22]. The calculated ΔG°_{ads} values are closer to -10 kJ mol⁻¹ indicating that the adsorption mechanism of the inhibitors on α -brass in 1 M HNO₃ solution was typical of physical adsorption. The unshared electron pairs in sulphur, nitrogen as well as in oxygen may interact with d-orbitals of Cu to provide a protective physical adsorbed film [23]. The values of thermodynamic parameter for the adsorption of inhibitors Table 5 can provide valuable information about the mechanism of corrosion inhibition. While an endothermic adsorption process ($\Delta H^{\circ}_{ads} > 0$) is attributed unequivocally to chemisorption [24], an exothermic adsorption process (ΔH°_{ads} for the adsorption of inhibitors in 1 M HNO₃ indicating that this inhibitor may be physically adsorbed. The ΔS°_{ads} values in the presence of inhibitors in 1 M HNO₃ are negative. This indicates that an increase in disorder takes places on going from reactants to the metal-adsorbed reaction complex [25].



Figure 3: Variation of ΔG^{o}_{ads} versus T for the adsorption of inhibitors on α -brass surface in 1 M HNO₃ at different temperatures

Table 5: Thermodynamic parameters for the adsorption of investigated compounds on α-brass surface in 1 M HNO₃ at different temperatures

Inhibitor	Temperature °C	K _{ads} x10 ⁻³ M ⁻¹	-∆G° _{ads} kJ mol ⁻¹	-ΔH° _{ads} kJ mol ⁻¹	-ΔS° _{ads} kJ mol ⁻¹
	25	1.34	10.7	82.3	240.5
А	30	1.38	10.9		235.7
	35	1.41	11.2		231.1
	40	1.43	11.4		226.7
	45	1.44	11.6		222.5
	25	1.37	10.7	79.1	229.3
В	30	1.40	11.0		224.8
	35	1.45	11.2		220.2
	40	1.46	11.4		216.1
	45	1.44	11.6		212.2
	25	1.45	10.9	72.6	207.2
C	30	1.40	11.0		203.4
	35	1.46	11.3		199.2
	40	1.46	11.4]	195.4
	45	1.47	11.6		191.7

Kinetic -thermodynamic corrosion parameter

The activation parameters for the corrosion process were calculated from Arrhenius-type plot according to eq. (6): $k_{corr} = A \exp \left(E_{a}^{*}/RT \right)$ (6)

where E_a^* is the apparent activation corrosion energy, R is the universal gas constant, T is the absolute temperature and A is the Arrhenius pre-exponential constant. Values of apparent activation energy of corrosion for α -brass in 1 M HNO₃ shown in Table 6, without and with various concentrations of compound (A) determined from the slope of log (k_{corr}) versus 1/T plots are shown in Figure 4. Inspection of the data shows that the activation energy is lower in the presence of inhibitors than in its absence. This was attributed to slow rate of inhibitor adsorption with a resultant closer approach to equilibrium during the experiments at higher temperatures according to Hoar and Holliday [26]. But, Riggs and Hurd [27] explained that the decrease in the activation energy of corrosion at higher levels of inhibition arises from a shift of the net corrosion reaction from the uncovered part of the metal surface to the covered one. Schmid and Huang [28] found that organic molecules inhibit both the anodic and cathodic partial reactions on the electrode surface and a parallel reaction takes place on the covered area, but the reaction rate on the covered area is substantially less than on the uncovered area similar to the present study. The alternative formulation of transition state equation is shown in Eq. (7):

 $k_{corr} = (RT/Nh)exp(\Delta S^*/R)exp(-\Delta H^*/RT)$

(7)

where k_{corr} is the rate of metal dissolution, 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 k against (1/T) in the case of inhibitor (A) in 1 M HNO₃. Similar behavior is observed in the case of inhibitor B and C (not shown). Straight lines are obtained with a slopes equal to $(\Delta H^*/2.303R)$ and intercepts are [log (R/Nh + $\Delta S^*/2.303R$)] are calculated Table 6.

The increase in E_a^* with increase inhibitor concentration Table 6 is typical of physical adsorption. The positive signs of the enthalpies (ΔH^*) reflect the endothermic nature of the brass dissolution process. Values of entropy (ΔS^*) imply that the activated complex at the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [29,30].



Figure 4: Log k vs. (1/T) curves for Arrhenius plots for α-brass corrosion rates (k_{corr}) after 120 minute of immersion in 1M HNO₃ in the absence and presence of various concentrations of inhibitor (A)



Figure 5: Log (k/T) vs. (1/T) curves for Transition plots for α-brass corrosion rates (k_{corr}) after 120 minute of immersion in 1M HNO₃ in the absence and presence of various concentrations of inhibitor (A)

Table 6: Activation parameters for α-brass corrosion in the absence and presence of brass corrosion in the absence and presence of various concentrations of investigated inhibitors in 1 M HNO₃

Inhibitor	[inh]x10 ⁶ M	Ea [*] kJ mol ⁻¹	ΔH [*] kJ mol ⁻¹	-ΔS [*] J mol ⁻¹ K ⁻¹	A x10 ⁷ g cm ⁻² min ⁻¹
Blank	0	4.47	1.52	149.03	2.358
A	1	4.55	1.98	102.47	3.044

	3	4.62	1.99	103.28	3.954
	5	4.87	2.00	104.52	5.991
	7	5.01	2.01	106.49	6.778
	9	5.28	2.02	109.98	11.323
	11	5.39	2.03	114.96	13.876
В	1	4.51	1.88	128.52	2.921
	3	4.53	1.92	128.53	3.028
	5	4.83	1.95	129.75	5.785
	7	4.92	1.96	129.79	6.290
	9	5.07	1.97	131.91	9.929
	11	5.26	1.99	133.18	11.353
C	1	4.49	1.55	133.38	2.557
	3	4.51	1.56	133.75	2.815
	5	4.79	1.57	135.21	3.458
	7	4.81	1.58	136.42	6.057
	9	5.00	1.59	136.46	6.539
	11	5.07	1.60	137.98	8.197

Potentiodynamic Polarization Measurements

Figures 6 show typical polarization curves for α -brass in 1 M HNO₃ media. The two distinct regions that appeared were the active dissolution region (apparent Tafel region), and the limiting current region. In the inhibitor-free solution, the anodic polarization curve of copper showed a monotonic increase of current with potential until the current reached the maximum value. After this maximum current density value, the current density declined rapidly with potential increase, forming an anodic current peak that was related to Cu (NO₃)₂ film formation. In the presence of inhibitor, both the cathodic and anodic current densities were greatly decreased over a wide potential range. Various corrosion parameters such as corrosion potential ($E_{corr.}$), anodic and cathodic Tafel slopes (β_a , β_c), the corrosion current density (i_{corr}), the degree of surface coverage (θ) and the inhibition efficiency (%IE) are given in Tables 7. It can see from the experimental results that in all cases, addition of inhibitors induced a significant decrease in cathode and anodic currents. The values of E_{corr} were affected and slightly changed by the addition of inhibitors. This indicates that these inhibitors act as mixed-type inhibitors. The slopes of anodic and cathodic Tafel lines (β_a and β_c), were slightly changed (Tafel lines are parallel), on increasing the concentration of the tested compounds which indicates that there is no change of the mechanism of inhibition in the presence and absence of inhibitors. The orders of inhibition efficiency of all inhibitors at different concentrations as given by polarization measurements are listed in Table 7. The results are in good agreement with those obtained from weight-loss measurements.



Figure 6: Potentiodynamic polarization curves for the dissolution of α- brass in 1 M HNO₃ in the absence and presence of different concentrations of compound (A) at 25 °C

coverage (0),	verage (0) , and minimum enciency (% i.e.) of α -brass in 1 M HNO ₃ at 25 C for compounds (A, B c								
Inhibitor	[inh] x10 ⁶ M	-E _{corr} mV vs SCE	i _{corr} μA cm ⁻²	β _a mV dec ⁻¹	β _c mV dec ⁻¹	θ	% IE		
Blank	0	3	914	57	189				
	1	10	600	51	222	0.343	34.3		
	3	13	218	273	223	0.761	76.1		
	5	19	165	44	180	0.819	81.9		
А	7	20	92.4	31	181	0.899	89.9		
	9	22	75.9	29	194	0.916	91.6		
	11	39	70.8	33	198	0.922	92.2		
	1	4	785	43	174	0.141	14.1		
	3	9	657	59	170	0.281	28.1		
	5	14	560	43	213	0.387	38.7		
В	7	15	357	70	167	0.609	60.9		
	9	27	354	72	167	0.612	61.2		
	11	35	191	52	200	0.791	79.1		
	1	3	806	44	177	0.118	11.8		
	3	4	658	60	171	0.280	28.0		
C	5	9	561	43	213	0.366	36.6		
U	7	27	439	57	150	0.519	51.9		
	9	35	420	60	196	0.541	54.1		
	11	175	350	60	176	0.617	61.7		

Table 7: Corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slopes (β_c , β_a), degree of surface coverage (θ), and inhibition efficiency (% IE) of α -brass in 1 M HNO₃ at 25°C for compounds (A, B & C)

Electrochemical impedance spectroscopy (EIS)

EIS is well-established and it is powerful technique for studying the corrosion. Surface properties, electrode kinetics and mechanistic information can be obtained from impedance diagrams [31-35]. Figure 8 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 25°C. The increase in the size of the capacitive loop with the addition of investigated

compounds shows that a barrier gradually forms on the α -brass surface. The increase in the capacitive loop size (Figure 8a) enhances, at a fixed inhibitor concentration, following the order: (A) > (B) > (C), confirming the highest inhibitive influence of compound (A). Bode plots (Figure 8b), 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 α -brass 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 [36] as well as to the inhomogenities of the surface.



Figure 7: Equivalent circuit model used to fit experimental EIS

EIS spectra of the investigated compounds were analyzed using the equivalent circuit, Figure 7, which represents a single charge transfer reaction and fits well with our experimental results. The constant phase element, CPE, is introduced in the circuit instead of a pure double layer capacitor to give a more accurate fit [37]. The double layer capacitance, C_{dl} , for a circuit including a CPE parameter (Y0 and n) were calculated from eq.8 [38]: $C_{dl} = Y_0 (\omega_{max})^{n-1}$ (8)

where Y_0 is the magnitude of the CPE, $\omega_{max} = 2\pi f_{max}$, 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 [39,40]. 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 [41]. From the impedance data Table 8, we concluded that the value of R_{ct} increases with increasing the concentration of the inhibitors and this indicates an increase in % IE_{EIS}, which in concord with the EFM results obtained. 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 [42, 43]. The inhibition efficiency was calculated from the charge transfer resistance data from eq.9 [44] : % IE_{EIS} = [1 - (R°_{ct}/ R_{ct})] ×100 (9)

where R^o_{ct} and Rct are the charge-transfer resistance values without and with inhibitor respectively



Figure 8a: The Nyquist plots for the corrosion of α-brass in 1M HNO₃ in the absence and presence of different concentrations of inhibitor (A) at 25 ° C



Figure 8b: The Bode plots for the corrosion of α-brass in 1 M HNO₃ in the absence and presence of different concentrations of inhibitor (A) at 25 °C

Table 8: Electrochemical kinetic parameters obtained by EIS technique for α-brass in 1 M HNO₃ without and with various concentrations of investigated compounds at 25°C

Inhibitor	[inh] x10 ⁶ M	$\frac{R_{ct}}{\Omega \ cm^2}$	${f R_s} \Omega {f cm}^2$	C _{dl} µFcm ⁻²	θ	% IE
Blank	0	195.7	1.024	5.197		
А	1	391.5	1.924	2.588	0.500	50.0
	3	772.8	1.526	1.312	0.746	74.6
	5	802.3	1.422	1.263	0.756	75.6
	7	826.4	2.047	1.227	0.763	76.3

	9	860.3	1.845	1.178	0.772	77.2
	11	1139	1.466	0.882	0.828	82.8
В	1	331.7	1.113	3.066	0.410	41.0
	3	348.3	1.088	2.915	0.438	43.8
	5	349.8	1.153	2.903	0.441	44.1
	7	371.1	1.318	2.738	0.473	47.3
	9	497.8	1.203	2.04	0.607	60.7
	11	568.7	1.222	1.7858	0.656	65.6
С	1	211.9	1.645	4.77	0.076	7.60
	3	223.9	1.563	4.52	0.126	12.6
	5	245.4	1.490	4.12	0.203	20.3
	7	273.4	1.529	3.706	0.284	28.4
	9	290.9	1.600	3.48	0.327	32.7
	11	331.9	1.568	3.05	0.410	41.0

Electrochemical Frequency Modulation

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 [45]. 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 9 shows the EFM Intermodulation spectra (current vs frequency) of α -brass in HNO₃ solution containing different concentrations of compound (A). Similar curves were obtained for compound (B & C) (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 [46]. 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 9. The data presented in Table 9 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 α -brass in 1 M HNO₃ 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 Eq. (10):

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

(10)

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: A > B > C.

Inh	[inh]x10 ⁶ M	i _{corr} μAcm ⁻²	β _a mVdec ⁻¹	$egin{array}{c} \beta_c \ mVdec^{-1} \end{array}$	CF-2	CF-3	C.R mpy	θ	% IE
Blank	0	70.03	64.	115	1.858	2.924	34.56	-	-
A	1	36.06	48	63	2.051	2.844	17.79	0.485	48.5
	3	20.54	59	122	1.944	2.611	10.13	0.706	70.6
	5	20.22	76	179	2.086	2.531	9.977	0.711	71.1
	7	20.16	70	147	1.972	3.626	9.94	0.712	71.2
	9	19.79	63	125	1.957	2.551	9.768	0.717	71.2
	11	14.79	75	133	2.428	2.851	7.296	0.788	78.8

Table 9: Electrochemical kinetic parameters obtained from EFM technique for α-brass in 1 M HNO₃ in the absence and presence of different concentrations of compounds (A,B and C)

В	1	41.19	60	135	1.969	2.65	20.33	0.412	41.2
	3	34.21	53	69	1.98	2.916	16.88	0.511	51.1
	5	33.46	50	73	1.678	3.578	16.51	0.522	52.2
	7	31.89	51	68	1.938	2.875	15.74	0.545	54.5
	9	27.49	58	87	2.11	3.147	13.54	0.607	60.7
	11	25.42	62	98	2.044	2.86	12.54	0.637	63.7
С	1	66.6	58	122	1.854	2.481	32.86	0.048	4.80
	3	64.93	55	117	1.796	3.228	32.04	0.073	7.30
	5	58.38	67	165	1.902	2.405	28.81	0.166	16.6
	7	56.58	58	120	2.031	2.994	27.94	0.192	19.2
	9	53.08	61	124	1.823	3.012	26.19	0.242	24.2
	11	37.38	58	99	1.939	3.097	18.45	0.466	46.6



Figure 9: EFM spectra for α-brass in 1 M HNO₃ in the absence and presence of different concentrations of compound (A) at 25 ° C

SEM/EDX examination

In order to verify if the investigated compounds molecules are in fact adsorbed on α -brass surface, both SEM and EDX experiments were carried out. The SEM micrographs for α -brass surface alone and after 24 h immersion in 1 M HNO₃ without and with the addition of 11 x 10⁻⁶ M of the investigated compounds are shown in Figures (10a-e). The corresponding EDX profile analyses are presented in Figures (11a-e). As expected, Figure 10a shows metallic surface is clear, while in the absence of the investigated compounds, the α -brass surface is damaged by HNO₃ corrosion (Figure 10b). In contrast, in presence of the investigated compounds (Figures (10c-e)), the metallic surface seems to be almost no affected by corrosion. The corresponding EDX data are presented in Figures (11a-e) and Table 10. It is clear from the EDX spectra of α -brass in the presence of investigated compounds, the existence of C and O peaks (Figures(11c-e)) which suggest the adsorption of investigated compounds on the α -brass surface and confirm the formation of a thin film of investigated compounds observed in SEM micrograph, thus protecting the surface against corrosion.





Figure 20: SEM micrographs of α-brass surface (a) before of immersion in 1 M HNO₃, (b) after 24 h of immersion in 1 M HNO₃, (c) after 24 h of immersion in 1 M HNO₃+ 11x10⁻⁶ M of compound A, (c) after 24 h of immersion in 1 M HNO₃+ 11x10⁻⁶ M of compound B and (c) after 24 h of immersion in 1 M HNO₃+ 11x10⁻⁶ M of compound C at 25±1 °C.





Figure 11: EDX spectra of of α-brass surface (a) before of immersion in 1 M HNO₃, (b) after 24 h of immersion in 1 M HNO₃, (c) after 24 h of immersion in 1 M HNO₃+ 11x10⁻⁶ M compound A, (c) after 24 h of immersion in 1 M HNO₃+ 11x10⁻⁶ M compound B and (c) after 24 h of immersion in 1 M HNO₃+ 11x10⁻⁶ M compound C at 25°C

Table 10: Surface composition (weight %) of α-bass before and after immersion in 1 M HNO ₃ without and	ł
with 11×10^{-6} M of the investigated compounds at 25° C	

(Mass %)	Cu	Zn	Fe	С	0	Al	As	Sn	Si	S
Free	60.78	32.72	0.79	3.48	1.13	0.70	0.40			
Blank	54.57	25.78	0.78	10.41	7.85		0.61			
compound A	56.00	29.62	0.25	8.38	5.12			0.44	0.19	
compound B	55.28	27.85	0.51	10.42	5.28	0.37				0.29
compound C	55.06	28.29		9.00	7.39				0.26	

Quantum calculation

The E_{HOMO} indicates the ability of the molecule to donate electrons to an appropriated acceptor with empty molecular orbitals, whereas the E_{LUMO} indicates its ability to accept electrons. The lower the value of E_{LUMO} , the more ability of the molecule is to accept electrons [47].

The higher the value of E_{HOMO} of the inhibitor, the easier is its ability to offer electrons to the unoccupied d-orbital of metal surface, and the greater is its inhibition efficiency. As is seen from Table 10, compound A has the highest value of E_{HOMO} , which indicate that this molecule has high capacities of charge donation to the metallic surface and has high inhibition efficiency. It was found that the variation of the calculated LUMO energies among all investigated inhibitors is rule less, and the inhibition efficiency is misrelated to the changes of the E_{LUMO} Table 10.

The HOMO-LUMO energy gap, ΔE approach, which is an important stability index, is applied to develop theoretical models for explaining the structure and conformation barriers in many molecular systems. The smaller the value of ΔE , the more is the probable inhibition efficiency the compound has [48-50]. It was shown from (Table 10) that compound A has the smallest HOMO-LUMO gap compared with the other molecules. Accordingly, it could be expected that compound (A) molecule has more inclination to adsorb on the metal surface than the other molecules. There is a general consensus by several authors that the more negatively charged hetero atom is the more is its ability to adsorb on the metal surface through a donor-acceptor type reaction [51,53]. Variation in the inhibition efficiency of the inhibitors depends on the presence of electronegative O- and N- atoms as substituent in their molecular structure. The calculated charges of selected atoms are presented in Figure 10.

Table 10: E _{HOMO} , E _{LUMO} , energy gap (ΔE) and molecular area for the different compounds as obtained (PM3)
method in gas phase

	(A)	(B)	(C)
-E _{HOMO}	8.87	8.959	9.17
-E _{LUMO}	1.361	1.337	1.441
ΔΕ	7.509	7.622	7.729



Figure 10: Optimized molecular structure of inhibitors (A, B and C), and their frontier molecular orbital density distribution (HOMO and LUMO)

Mechanism of Corrosion Inhibition

The inhibition mechanism involves the adsorption of the inhibitor on the metal surface immersed in aqueous HNO₃ solution. Four types of adsorption [54] may take place involving organic molecules at the metal–solution interface: 1)Electrostatic attraction between the charged molecules and the charged metal; 2) Interaction of unshared electron pairs in the molecule with the metal; 3) Interaction of π -electrons with the metal; 4) Combination of all the above. From the observations drawn from the different methods, corrosion inhibition of α -brass in 1M HNO₃ solutions by the investigated inhibitors as indicated from weight loss, potentiodynamic polarization and EIS techniques were found to depend on the concentration and the nature of the inhibitor. The order of inhibition efficiency is as follows: A > B > C. This order of decreased inhibition efficiency of the additives can be accounted for in terms of the polar effect [55] of the p-substituents on the benzoyl ring. Compound A is the most efficient inhibitor because of presence of highly electron releasing p-OH (σ = - 0.37) which enhances the delocalized π -electrons on the active centers of the compound, where σ is the substituent constant [55] and is a relative measure of the electron density at the reaction center. Compound B p-CH₃ (σ = - 0.17) comes next in the sequence of decreased inhibition efficiency. This is because p-CH₃ is lower in electron donation than p-OH. Compound C p-Br (σ = + 0.232) occupy the lowest compound in inhibition efficiency because p-Br group with highest electrophilic character imparts the lowest inhibition efficiency.

Conclusions

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

1- All the investigated compounds are good corrosion inhibitors for α-brass in 1 M HNO₃ solution.

2- The effectiveness of these inhibitors depends on their structures.

3- The variation in inhibitive efficiency depends on the type and the nature of the substituent present in the inhibitor molecule. Reasonably good agreement was observed between the values obtained by the weight loss and electrochemical measurements were in good agreement.

4- The order of % IE of these investigated compounds is in the following order: (A) > (B) > (C).

5- Results obtained from potentiodynamic polarization indicated that the investigated derivatives are mixed-type inhibitors.

6- Percentage inhibition efficiency of all investigated compounds was temperature dependent and its addition led to a decrease of the activation corrosion energy in all the studied acid media.

7- The thermodynamic parameters revealed that the inhibition of corrosion by investigated compounds is due to the formation of a physical adsorbed film on the metal surface.

8- The adsorption of all investigated compounds onto α -brass surface follows the Temkin adsorption isotherm model.

9- The positive values of the free energy of adsorption and adsorption heat are indicating that the process was spontaneous and endothermic

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