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New azonitrile derivatives as corrosion inhibitors for copper in nitric acid solution

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Abstract: The inhibitive effect of new synthesized azonitriles, namely 3-phenyl azo-2-amino-1,1,3-tricyano propene, 3-p-tolyl azo-2-amino-1,1,3-tricyano propene, 3-p-anisyl azo-2-amino-1,1,3-tricyano propene, 3-p-nitro phenyl azo-2 amino-1,1,3-tricyano propene, and 3-p-phenyl carboxylic azo-2-amino-1,1,3-tricyano propene on the corrosion of copper in nitric acid solution was investigated using chemical and electrochemical methods. The inhibition efficiency was found to increase with inhibitor concentration and decreased with rise in solution temperature. Various thermodynamic parameters were calculated and discussed in order to elaborate the mechanism of corrosion inhibition. Polarization measurements revealed that the studied azonitriles acted as mixed inhibitors. The results revealed that these compounds were adsorbed onto the copper surface and the adsorption obeyed the Temkin adsorption isotherm. The quantum chemical calculations were in good agreement with the experimental results.

Subjects: Chemistry; Material Science; Materials Science; Metals & Alloys; Physical Sciences

Keywords: corrosion; azonitrile derivatives; HNO₃; quantum chemical calculations

1. Introduction
Copper is widely used in many industrial applications in heating and in cooling systems for its high electrical, good corrosion resistance, mechanical workability, and excellent thermal conductivities. But can suffer severe corrosion in aerated acidic media. Hydrochloric acid typically is used in pickling baths because, unlike sulfuric acid, it can be regenerated. One of the most important methods in the corrosion protection of copper is the use of inhibitors. Organic compounds are successfully used in industries against acidic corrosion of metals (Negm & Zaki, 2009; Raman, Libene, & Quraishi, 2004). The presence of electron donating atoms in the organic compounds such as N, O, S is crucial for an efficient corrosion inhibitor. The corrosion efficiency of organic compounds is related to their adsorption properties such as the type of

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The author, A.S. Fouda is a full professor in Chemistry Department, Faculty of Science, Mansoura University, Egypt since 1988. His research area is the corrosion of metals, alloys, and their inhibition in all media using organic compounds and plant extracts. He published more than 300 research papers in international journals. He got his DSc in physical Chemistry 2013. His areas of research interest include corrosion, fuel cells, electro catalysis, electroplating, and green chemistry.

PUBLIC INTEREST STATEMENT
The purpose of this paper is to investigate the inhibitive effect of five azonitriles derivatives, namely 3-phenyl azo-2-amino-1,1,3-tricyano propene, 3-p-tolyl azo-2-amino-1,1,3-tricyano propene, 3-p-anisyl azo-2-amino-1,1,3-tricyano propene, 3-p-nitro phenyl azo-2 amino-1,1,3-tricyano propene, and 3-p-phenyl carboxylic azo-2-amino-1,1,3-tricyano propene on the copper corrosion in nitric acid solution. HNO₃ is an oxidizing agents used in many industries. The results obtained showed that these derivatives are good corrosion inhibitors for copper corrosion in HNO₃ solution and may be used as inhibitors in industries.
corrosive medium, the nature and state of the metal surface, and on chemical structure of the inhibitor (Azazi, Celen, Namlil, & Turhani, 2007). Nowadays, many studies indicate that nitrogen-containing organic compounds are found to behave better for the metals corrosion in hydrochloric acid than in sulfuric acid. The possible reason is that there is a synergism inhibition between chloride ion and nitrogen-containing organic compound for metal corrosion in hydrochloric acid. Generally speaking, organic inhibitors are found to protect metal corrosion in acid solutions by adsorbing on metal surface. Adsorption isotherms such as the Langmuir adsorption isotherm are used to elucidate the inhibition mechanism of inhibitors. So, the use of organic compounds has been studied extensively (Fouda, Abdallah, & El-Dahab, 2010; Frignani, Fonsati, Monticelli, & Brunoro, 1999; Larabi, Benoli, & Harek, 2006; Sankarapapavinassam & Ahmed, 1992; Tang et al., 2010; Vastag, Szacs, Shaban, & Kalman, 2001; Yu, Feng, & Yu, 2009; Zhang, Gao, & Zhou, 2005). Several mechanisms have been proposed to explain the function of corrosion inhibitors of which the adsorption theory is the most pertinent (Hackerman & Hurd, 1961). 3-benazidinophodanine (Mohammed, 1983), substituted phenols (Fouda & Mohamed, 1988; Fouda, Gomma, & Moussa, 1992) 2-hydroxycetophenone-aroyl hydrazone derivatives (Fouda, Gouda, & Abd El-Rahman, 2000), natural honey (El-etrie, 1998), n-decylamine (Riggs & Hurd, 1967), benzamido rhodanines (Fouda, Moussa, Taha, & Mohamed, 1989), Ortho-substituted anilines (Khaled & Hackerman, 2004), benzoyl benzaldehyde hydrazone derivatives (Abd El-Maksoud, El-Shafei, Mostafa, & Fouda, 1995), and ethylamine (Fouda & Mohamed, 1990) also, have been used as effective acid corrosion inhibitors.

This paper aimed to study the corrosion inhibition of copper in HNO₃ solution by some new synthesized azonitriles derivatives using weight loss, and galvanostatic polarization methods

2. Experimental procedures

2.1. Materials
Copper test samples containing 0.001% Sn, 0.001% Ag, 0.01% Fe, 0.0005% Bi, 0.002% Pb, and 0.0002% as and balance Cu were used for the tests. All chemicals were AR quality. A solution of 2 M HNO₃ was prepared with double distilled water.

2.2. Synthesis of inhibitors
A suspension of aromatic amine (I-V) (0.01 mol) in a mixture of water (10 ml) and concentrated HCl (× ml) was cooled in an ice bath and treated with a solution of sodium nitrite (0.69 g; 0.01 mol) in water (1 ml). The suspension dissolved slowly with stirring during 20 min. The solution was added portionwise to a stirred mixture obtained by dissolving malononitrile dimer (1.32 g; 0.01 mol) in water (2 ml) and ethanol (12 ml), adding sodium acetate (0.5 g) and crushed ice (Table 1). Overnight, a crystalline compound was collected with suction, washed with water and dried in air. Their melting points were measured and were found (more than 300°C) as reported before (Orban, 2005).

It has been found that, 2-amino-1,1,3-tricyanopropene (1) was coupled with aryl diazonium chloride to afford a product, which was considered to have structure (L). The structure of compounds (L₁–L⁵) was established by IR spectrum which showed absorption bands near 3,400–3,300 (NH₂), 2,220 (conjugated CN), 1,640 (–C=C–N–) and 1,600 cm⁻¹ (–N=N). In addition, the mass spectra of compounds (L₁–L⁵) give a more confirmation of their correct structures.
The inhibitors used are 3-arylazo-2-amino-1,1,3-tricyanopropene derivatives (L₁–L₅).

2.3. Solutions
The solution of two M HNO₃ was prepared with double distilled water, and its concentration was checked using standard NaOH solution. One hundred milliliter stock solutions (10⁻³ M) of compounds (L₁–L₅) were prepared by dissolving an accurately weighed quantity of each material in an appropriate volume of absolute ethanol, then the required concentrations (1 × 10⁻⁶–2 × 10⁻⁶ M) were prepared by dilution with double distilled water.

2.4. Methods

2.4.1. Weight loss technique
For weight loss measurements, the tested specimens were used in the form of sheets of dimensions 2 × 2 × 0.1 cm. The specimens were abraded by 2/0 and 3/6 emery papers, degreased with acetone, then washed with double distilled water, and finally dried between two filter papers. This treatment was carried out immediately before each measurement. The test pieces were suspended by suitable glass hooks at the edge of a beaker (6 cm inner diameter and having a total volume of 250 ml) and under the surface of the solution by about 1 cm. After certain period, three test pieces were taken out of the solution, rinsed by double-distilled water, dried and weighed again and the mean value of weight loss has been reported. The inhibitive efficiency (percentage IE) was calculated employing the formula:

Table 1. Names, structures, and nomenclature of investigated azonitrile derivatives

| Inhibitor | Aromatic amines | X, ml | Structure | Nomenclature |
|-----------|-----------------|-------|-----------|--------------|
| L₁        | I-Aniline       | 2     | ![Structure](image) | 3-phenyl azo-2-amino-1,1,3-tricyano propene |
| L₂        | II-p-toluidine  | 2     | ![Structure](image) | 3-p-tolyl azo-2-amino-1,1,3 tricyano propene |
| L₃        | III-p-anisidine | 2     | ![Structure](image) | 3-p-anisyl azo-2-amino-1,1,3 tricyano propene |
| L₄        | IV-p-nitroaniline | 20 | ![Structure](image) | 3-p-nitro phenyl azo-2-amino-1,1,3 tricyano propene |
| L₅        | V-p-amino benzoic acid | 4 | ![Structure](image) | 3-p-phenyl carboxylic azo-2-amino-1,1,3 tricyano propene |
where \( W_B \) = weight loss in 2 M HNO\(_3\) solution and \( W_I \) = weight loss in inhibited solution. \( \Theta \) is the degree of surface coverage.

2.4.2. Galvanostatic polarization method

For electrochemical measurements, the electrodes used for these experiments were cut from a wire of diameter 0.037 cm. A copper wire was fixed at one end by mechanical jamming, and the electrode was fixed into a Pyrex glass tubing by means of araldite (Ciba-Geigy Switzerland) leaving an exposed length of 1 cm in contact with the solution. A silver-silver chloride and platinum were used as reference and auxiliary electrodes, respectively. Currents from constant current device were measured with a multimeter with an accuracy of ± 4%. Corrosion potentials were recorded using a digital ionalizer device (Orion model 701 A). The potential at any given current under similar experimental conditions was reproducible within ± 3%. The detailed experimental procedure has been given elsewhere (Fouda et al., 2000). The inhibitive efficiency (percentage IE) was calculated employing the formula:

\[
\text{\% IE} = \left[1 - \left( \frac{W_I}{W_B} \right) \right] \times 100
\]

(1)

\[
\theta = \left[1 - \left( \frac{W_I}{W_B} \right) \right]
\]

(2)

\[
\text{\% IE} = \left[1 - \left( \frac{i_{\text{inh}}}{i_{\text{free}}} \right) \right] \times 100
\]

(3)

\[
\theta = \left[1 - \left( \frac{i_{\text{inh}}}{i_{\text{free}}} \right) \right]
\]

(4)

where \( i_{\text{inh}} \) and \( i_{\text{free}} \) are the corrosion current with and without inhibitor, respectively.
3. Results and discussion

3.1. Weight loss measurements

Figure 1 shows the weight loss-time curves for copper in 2 M HNO₃ and in the presence of different concentrations of inhibitor L³ (the most efficient one). Curves are characterized by gradual rise in weight loss with time. The curves indicate that, the weight loss of copper depends on the concentration of additives (Table 2). Increase in bulk concentration and consequently increase in surface coverage by the additive increases their inhibition efficiency as indicated by the decrease in weight loss per cm².

Table 2 shows the effect of concentrations of the inhibitors on percentage inhibition efficiency. From these data, one can say that the order of the inhibition efficiency of these inhibitors is L³ > L² > L¹ > L⁵ > L⁴.

3.2. Effect of temperature

The effect of temperature on the corrosion rate of copper in 2 M nitric acid solution in the absence and presence of 1 × 10⁻⁶ to 21 × 10⁻⁶ M of these inhibitors was studied at different temperatures (30–50°C) by weight loss measurements. The data of Table 3 show the percentage inhibition efficiency of investigated compounds at different temperatures. From these results, one can conclude that as the temperature raises the percentage inhibition efficiency decreases. This indicates that the adsorption of these compounds on copper surface is physical.

### Table 2. Variation in the percentage inhibition efficiency (% IE) of some azonitrile derivatives with their concentrations from weight loss method at 30°C and after 60 min immersion

| Concentration, (M) | % IE |
|--------------------|------|
|                    | L³   | L²   | L¹   | L⁵   | L⁴   |
| 1 × 10⁻⁶           | 59.4 | 57.0 | 56.7 | 54.0 | 45.9 |
| 5 × 10⁻⁶           | 63.0 | 62.4 | 60.3 | 57.1 | 53.7 |
| 9 × 10⁻⁶           | 64.1 | 63.3 | 62.4 | 58.9 | 56.1 |
| 13 × 10⁻⁶          | 68.7 | 68.0 | 63.4 | 61.9 | 58.2 |
| 17 × 10⁻⁶          | 70.6 | 69.6 | 67.3 | 64.3 | 62.9 |
| 21 × 10⁻⁶          | 74.9 | 74.6 | 70.8 | 65.8 | 64.7 |

### Table 3. Inhibition efficiency (% IE) of some azonitrile derivatives for copper dissolution in 2 M HNO₃ at different temperatures and different inhibitor concentrations (at 60 min immersion)

| Concentration, (M) | Temperature, °C | % IE |
|--------------------|-----------------|------|
|                    | Inhibitor       | L³   | L²   | L¹   | L⁵   | L⁴   |
| 13 × 10⁻⁶          | 30              | 68.7 | 68.0 | 63.4 | 61.9 | 58.2 |
|                    | 35              | 65.5 | 61.7 | 59.7 | 58.8 | 54.8 |
|                    | 40              | 56.5 | 54.5 | 49.6 | 49.0 | 39.0 |
|                    | 45              | 46.6 | 45.7 | 42.2 | 36.0 | 30.3 |
|                    | 50              | 40.7 | 34.5 | 31.2 | 25.3 | 14.1 |
| 21 × 10⁻⁶          | 30              | 74.9 | 74.6 | 70.8 | 65.8 | 64.7 |
|                    | 35              | 69.1 | 67.7 | 65.2 | 65.0 | 60.7 |
|                    | 40              | 61.4 | 60.3 | 58.8 | 49.9 | 40.8 |
|                    | 45              | 50.9 | 47.3 | 45.7 | 44.2 | 34.4 |
|                    | 50              | 49.7 | 41.4 | 39.1 | 33.2 | 29.1 |
Arrhenius plot of logarithmic of corrosion rate (k) against the reciprocal of absolute temperature (1/T) is shown graphically in Figure 2 at 21 \times 10^{-6} \text{ M} of the inhibitors, as shown from this figure, straight lines were obtained according to Arrhenius-type equation:

\[
K = A \exp \left(-\frac{E_a^*}{RT}\right)
\]  

(5)

where \(E_a^*\) is the activation energy, R universal gas constant, A is a constant that depends on a metal type and electrolyte and T is the absolute temperature. The values of activation energies, \(E_a^*\), were calculated and are given in Table 4. These values indicate that the presence of these inhibitors increases the activation energy of the metal dissolution reaction and that the process is diffusion controlled (\(E_a^* > 40 \text{ kJ mol}^{-1}\)). The increased activation energy, \(E_a^*\), in inhibited solutions compared to the blank suggests that the inhibitor is physically adsorbed on the corroding metal surface while either unchanged or lower \(E_a^*\) in the presence of inhibitor suggest chemisorptions (Fouda, Al-Sarawy, & El-Katori, 2006). It is seen from Table 4 that \(E_a^*\) values were higher in the presence of the additives compared to that in their absence, hence leading to reduction in corrosion rates. It has been suggested that adsorption of an organic inhibitor can affect the corrosion rate by either decreasing the available reaction area or by modifying the \(E_a^*\) of the anodic or cathodic reactions occurring in the inhibitor-free surface in the course of the inhibited corrosion process (Martinez & Metikoš-Huković, 2003). The \(E_a^*\) values support the earlier proposed physisorption mechanism. Hence, corrosion inhibition is assumed to occur primarily through physical adsorption on the Cu surface, giving rise to the deactivation of these surfaces to hydrogen atom recombination. Similar results have been reported in the earlier publications (Assaf, Abou-Krish, El-Shahawy, Makhlouf, & Soudy, 2007; Fouda et al., 2006).

The value of activation energy obtained in free acid solution is equal to 29.1 \text{ kJ mol}^{-1} which is in good agreement with the work of Fouda et al. who found that the activation energy of copper in 3 \text{ M} \text{ HNO}_3 is equal to 30.6 \text{ kJ mol}^{-1} (Fouda et al., 2000), but Tang et al. found that the activation energy of
copper dissolution in 1 M HCl is equal to 86.6 kJ mol\(^{-1}\) and in 0.5 M H\(_2\)SO\(_4\) is equal to 45.7 kJ mol\(^{-1}\) (Tang et al., 2010). By plotting log k/T vs. 1/T at 21 \times 10^{-6} M of these inhibitors, straight lines were obtained (Figure 3) according to transition state equation:

\[
\text{Rate}(k) = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right)
\]

where \(h\) is Planck’s constant, \(N\) is Avogadro’s number, \(\Delta H^*\) is the activation enthalpy, and \(\Delta S^*\) is the activation entropy. The values of \(\Delta H^*\) and \(\Delta S^*\) can be calculated from the slope and intercept of the above plot, respectively. The positive values of \(\Delta H^*\) indicates that the corrosion process is an endothermic one and the increase in the activation enthalpy in the presence of inhibitors implies that the addition of inhibitors to the acid solution increases the height of the energy barrier of the corrosion reaction to an extent that depends on the type and concentration of the present inhibitor. The entropy of activation (\(\Delta S^*\)) in the blank and inhibited solutions is large and negative indicating that the activated complex represents association rather than dissociation step (Hammett, 1940; Singh, Jha, & Verkey, 1990).

### 3.3. Adsorption isotherms

The values of degree of surface coverage, \(\theta\), for different concentrations of inhibitors have been employed and are useful in discussing the adsorption process. The degree of surface coverage, \(\theta\), was calculated using Equation (2).

Attempts were made to fit the, \(\theta\) values to different adsorption isotherms and correlation coefficients (\(R^2\)) were used to determine the best fits. By far, best results were obtained for Temkin adsorption isotherm. Figure 4 shows the plot of \(\theta\) against log C for copper dissolution in 2 M HNO\(_3\) in the presence of investigated compounds. Linear plots were obtained which indicate that the experimental data obtained obeys Temkin adsorption isotherm given by:

\[
\theta = \frac{1}{f} \ln K + \frac{1}{f} \ln C
\]

where \(f\) is the Temkin heterogeneity factor which related to Frumkin lateral interaction factor \(a\) (\(f = -2a\)). The factor \(a\) describes the molecular interactions in the adsorbed layer. The positive values of “\(a\)” indicates attraction forces between the adsorbed molecules while the negative values indicates repulsive forces between the adsorbed molecules. \(K\) is the equilibrium constant of adsorption process and \(C\) is the inhibitor concentration. The value of \(K\) is related to the free energy of adsorption \(\Delta G^\circ\) by the equation:

\[
K = \frac{1}{55.5} \exp\left[\frac{\Delta G^\circ_{\text{ads}}}{RT}\right]
\]

The adsorption parameters from Temkin adsorption isotherm are estimated and listed in Table 5. The high value of \(K\) reflects the high adsorption ability of these inhibitors on copper surface. The value of \(K\) was found to be in the order: \(L^1 > L^2 > L^3 > L^4 > L^5\) which runs parallel to the % IE. The

| Inhibitors | Activation parameters |
|-----------|-----------------------|
|           | \(E^*, \text{kJ mol}^{-1}\) | \(\Delta H^*, \text{kJ mol}^{-1}\) | \(-\Delta S^*, \text{J mol}^{-1} \text{K}^{-1}\) |
| Blank     | 29.1                  | 27.9                   | 179.3               |
| L\(^4\)   | 54.9                  | 52.3                   | 181.2               |
| L\(^1\)   | 56.8                  | 54.2                   | 182.6               |
| L\(^3\)   | 57.5                  | 54.9                   | 183.0               |
| L\(^3\)   | 58.1                  | 55.3                   | 183.5               |
| L\(^3\)   | 59.4                  | 56.8                   | 184.2               |

**Table 4. Activation parameters for the dissolution reaction of copper in 2 M HNO\(_3\) in the absence and presence of 21 \times 10^{-6} M azonitrile derivatives**
correlation coefficients are very good and very close to unity indicating that the adsorption of these compounds followed Temkin adsorption isotherm. Also, the values of \( a \) are negative in all cases showing that repulsion exists in the adsorption layer (Tang, Li, Si, Mu, & Liu, 2006). In acid solution, these inhibitors may exist in both protonated and molecular species which can affect the corrosion process to different extents, depending on their relative proportion. Physical adsorption is a result of electrostatic attraction between charged metal surface and protonated species in the bulk solution. Though physisorption of the protonated species by the electrostatic interaction with chloride ion adsorbed on the copper surface should prevail, the observed adherence to the Temkin adsorption isotherm suggests the participation of some molecular species. The negative value of \( \Delta G_{\text{ads}} \) indicates spontaneous adsorption of investigated compounds on copper surface and also the strong interaction between inhibitor molecules and the metal surface (Bayol, Gurten, Dursun, & Kayakirilmaz, 2008). Generally, the standard free energy values of −20 kJ mol\(^{-1}\) or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface (physical adsorption), those of −40 kJ mol\(^{-1}\) or more negative involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate covalent bond (chemical adsorption) (Abiola & Oforka, 2004). The calculated standard free energy of adsorption value is close to −40 kJ mol\(^{-1}\). Therefore, it can be concluded that the adsorption value is more chemical than physical adsorption (Li, Deng, Fu, & Li, 2009) i.e. mixed one.

### 3.4. Galvanostatic polarization method

Both the anodic and cathodic polarization curves of copper in 2 M HNO\(_3\) in the absence and presence of different concentrations of compound (L\(^3\)) are shown in Figure 5. It is clear that the polarization behavior of copper in this media follows almost a similar pattern. Various corrosion kinetic parameters such as corrosion potential \( (E_{\text{corr}}) \), corrosion current \( (i_{\text{corr}}) \), and Tafel slopes \( (\beta_a \text{ and } \beta_c) \), degree of surface coverage \( (\Theta) \) and % inhibition efficiency (% IE) derived from the polarization curves are given.
in Table 6. From these data, one can say that these compounds behave as mixed-type inhibitors, because the potential shift in the cathodic direction is comparable with that in the anodic direction. The decrease in \(i_{\text{corr}}\) with increase in additive concentration demonstrates the efficiency of the tested material as a corrosion inhibitor. The measured free corrosion potential in 2 M HNO\(_3\) solution is 43.4 mV vs. SCE in satisfactory agreement with published results (Fouda, Abd, & Kandil, 2005; Fouda et al., 2000). The approximately constant value of \(E_{\text{corr}}\) suggests that inhibition takes place by simple blocking of the electrode surface.

Table 7 shows the variation in the percentage inhibition efficiency of these compounds with their concentrations obtained from polarization method at 30°C. The order of decreasing inhibition efficiency of these compounds is: \(L^3 > L^2 > L^1 > L^5 > L^4\) and is in good agreement with that obtained from weight loss technique.
3.5. Theoretical study

Recently, it has been reported that the computational methods have potential application towards the design and development of organic compounds containing hetero-atoms as corrosion inhibitors for metals (Ju, Kai, & Li, 2008). The major thrust of quantum chemical research is to understand and explain the functions of these heterocyclic compounds in molecular terms in order to support experimental data obtained from various measurements.

It had reported that the $E_{\text{HOMO}}$ often associated with the electron donating ability of the molecule and the higher corrosion inhibition efficiency. High values of $E_{\text{HOMO}}$ indicate a tendency of the molecule to donate electrons to act with acceptor molecules with low energy, empty molecular orbital.

Table 6. The effect of compound (L3) concentrations on the free corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), Tafel slopes ($\beta_a$ and $\beta_c$), inhibition efficiency (% IE), and degree of surface coverage ($\theta$) of copper in 2 M HNO₃ at 30°C

| Concentration, (M) | $E_{corr}$, mV | $i_{corr}$, $\mu$A cm⁻² | $\beta_a$, mV dec⁻¹ | $\beta_c$, mV dec⁻¹ | $\theta$ | % IE  |
|-------------------|----------------|--------------------------|----------------------|----------------------|---------|------|
| 0.0               | 43.4           | 316.2                    | 60                   | 109                  | -       | -    |
| $1 \times 10^{-6}$| 48.5           | 125.9                    | 63                   | 114                  | 0.602   | 60.2 |
| $5 \times 10^{-6}$| 49.2           | 115.3                    | 65                   | 115                  | 0.635   | 63.5 |
| $9 \times 10^{-6}$| 49.2           | 109.9                    | 67                   | 117                  | 0.652   | 65.2 |
| $13 \times 10^{-6}$| 49.2           | 96.0                     | 68                   | 120                  | 0.696   | 69.6 |
| $17 \times 10^{-6}$| 50.3           | 90.7                     | 70                   | 122                  | 0.713   | 71.3 |
| $21 \times 10^{-6}$| 51.6           | 75.5                     | 73                   | 124                  | 0.761   | 76.1 |
Similarly, the ELUMO represents the ability of the molecule to accept electrons. The lower ELUMO values, the easier the acceptance of electrons from metal surface, (Ozcan & Dehri, 2004), as the $\Delta E_{L-H}$ (energy gap) decreased, interactions between the reacting species become stronger and as a result, efficiency of inhibitors improved. Quantum chemical properties listed in Table 8 revealed that the investigated inhibitors have high $E_{\text{HOMO}}$, low $E_{\text{LUMO}}$, and low $\Delta E_{L-H}$. These values were in accordance with high inhibition efficiency and run parallel to % IE of these compounds. The optimized molecular structure with Mullikan atomic charges of investigated compound is given in Figure 6.

### Table 7. Variation in the percentage inhibition efficiency (% IE) of some azonitrile derivatives with their concentrations obtained from polarization method at 30°C

| Concentration, (M) | % IE | L1 | L2 | L3 | L4 |
|--------------------|------|----|----|----|----|
| 1 $\times$ 10$^{-6}$ | 60.2 | 58.3 | 57.4 | 54.8 | 46.9 |
| 5 $\times$ 10$^{-6}$ | 63.5 | 62.7 | 61.2 | 58.7 | 54.9 |
| 9 $\times$ 10$^{-6}$ | 65.2 | 63.9 | 63.0 | 60.2 | 57.8 |
| 13 $\times$ 10$^{-6}$ | 69.6 | 68.4 | 64.2 | 62.9 | 59.2 |
| 17 $\times$ 10$^{-6}$ | 71.3 | 70.9 | 68.3 | 65.1 | 63.5 |
| 21 $\times$ 10$^{-6}$ | 76.1 | 75.6 | 72.0 | 67.0 | 65.6 |

### Table 8. The calculated quantum chemical properties for investigated compounds by PM6

| Compound | $-E_{\text{HOMO}}$ | $-E_{\text{LUMO}}$ | $\Delta E_{L-H}$ |
|----------|-------------------|------------------|-----------------|
| L1       | 9.941             | 1.367            | 8.574           |
| L2       | 9.617             | 1.234            | 8.383           |
| L3       | 9.251             | 1.194            | 8.057           |
| L4       | 10.272            | 1.924            | 8.348           |
| L5       | 10.194            | 1.924            | 8.270           |

Similarly, the $E_{\text{LUMO}}$ represents the ability of the molecule to accept electrons. The lower $E_{\text{LUMO}}$ values, the easier the acceptance of electrons from metal surface, (Ozcan & Dehri, 2004), as the $\Delta E_{L-H}$ (energy gap) decreased, interactions between the reacting species become stronger and as a result, efficiency of inhibitors improved. Quantum chemical properties listed in Table 8 revealed that the investigated inhibitors have high $E_{\text{HOMO}}$, low $E_{\text{LUMO}}$ and low $\Delta E_{L-H}$. These values were in accordance with high inhibition efficiency and run parallel to % IE of these compounds. The optimized molecular structure with Mullikan atomic charges of investigated compound is given in Figure 6.

#### 3.6. Mechanism

The adsorption of azonitrile derivatives can be attributed to the presence of polar unit having atoms of nitrogen and aromatic/heterocyclic rings (Abd El-Maksoud & Hassan, 2007). Therefore, the possible reaction centers are unshared electron pairs of heteroatoms and π-electrons of aromatic ring. It is well known that the inhibitors which not only offer d-electrons but also have unoccupied orbitals, exhibit a tendency to accept electrons from d-orbital of metal to form stable chelates which are considered as excellent inhibitor (Li et al., 1999).

Substitution of the hydrogen atom in the p-position in phenylhydrazo group at C-3 of compound (L1) by a methoxy and methyl groups in compounds (L3) and (L4), respectively, leads to an increase in protection efficiency. This behavior can be discussed on the basis that introducing the nucleophilic group (–CH$_3$ or –OCH$_3$) to the molecule increases the electron density of the surface active center of the molecule (–N–) and gives strong adsorption, and hence more inhibition, while the substitution of the hydrogen atom in compound (L1) by a carboxylic and nitro groups in compounds (L5) and (L4), respectively, leads to an decrease in protection efficiency. This behavior can be discussed on the basis that introducing the electrophilic group (–COOH or –NO$_2$) to the molecule decreases the electron density of the surface active center of the molecule (–N–) and gives less adsorption and hence less inhibition. The order of inhibition efficiency of this group: L3 > L2 > L1 > L5 > L4. This order can be interpreted according to the value of Hammett constants ($\sigma$).
3.7. Comparison of IE of the inhibitors in acid medium

The results obtained from the polarization and weight loss methods in 2 M HNO₃ on copper corrosion were in good agreements. The difference in % IE obtained from the two methods could be attributed to the weight loss method, the corrosion rate was determined chemically, independent of the electrode potential, and it is time-consuming, but in the polarization method, the corrosion rate depends on the operational potential and it is not time-consuming.

4. Conclusions

Based on the results obtained from the weight loss and electrochemical study, it can be concluded that:
(1) Azonitrile derivatives act as good corrosion inhibitors for copper in nitric acid solution.

(2) Inhibition efficiency increases with increasing inhibitor concentration, and the maximum % IE of 2.1 × 10^{-8} M of azonitrile derivatives reached 76.1%.

(3) The inhibition action of the azonitrile derivatives was attributed to mixed adsorption (physical and chemical) of these derivatives on copper surface, since $\Delta G_{ads}^\circ$ values are less than 40 kJ mol^{-1} and more than 20 kJ mol^{-1}.

(4) The % IE values increased with increasing inhibitor concentration but decreased with rising temperature.

(5) The adsorption of azonitrile derivatives on copper surface obeys the Temkin adsorption isotherm. The adsorption process is a spontaneous one since the sign of $\Delta G_{ads}^\circ$ is negative.

(6) Azonitrile derivatives act as mixed-type inhibitors in 2 M HNO_{3} solution.

(7) The weight loss and polarization methods were in good agreement.

(8) Quantum chemical parameters were found to give good correlation with experimentally determined inhibition efficiency.

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