Guanidine derivative as a new corrosion inhibitor for copper in 3% NaCl solution

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The effect of a new corrosion inhibitor namely, N-(5,6-diphenyl-4,5-dihydro-[1,2,4]triazin-3-yl)-guanidine (NTG) has been synthesized and its inhibitive performance towards the corrosion of copper in neutral solution of 3% NaCl has been investigated. Corrosion inhibition was studied by chemical method (weight loss) and electrochemical techniques including potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM). These studies have shown that NTG was a very good inhibitor and the inhibition efficiency up to 99% in 3% NaCl is obtained. Data obtained from EIS were analyzed to model the corrosion inhibition process through equivalent circuit. Comparable results were obtained by different chemical and electrochemical methods used. The adsorption of the inhibitor on the copper surface in the acid solution was found to obey Langmuir’s adsorption isotherm.

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1. Introduction

Copper has been one of the most important metals in industry owing to its high electrical and thermal conductivities, mechanical workability and its relatively noble properties. It is widely used in many applications in electronic industries and communications as a conductor in electrical power lines, pipelines for domestic and industrial water utilities including sea water, heat conductors, heat exchangers, etc. For this reason, corrosion of copper and its inhibition in a wide variety of media, particularly when they contain chloride ions, have attracted the attention of many investigators [1–8].

There are two main reasons for the considerable interest in this area. Firstly, chloride ions are very aggressive ions to copper and its alloys. This is due to the tendency of the chloride ion to form an unstable film, CuCl and soluble chloride complexes, CuCl$_2^-$, CuCl$_2$$_2^-$ [9]. Copper is so sensitive to chloride ions, and even trace amounts of Cl$^{-}$ ions can cause corrosion problem. Secondly, copper and its alloys are almost exclusively used for piping and delivery of water for domestic and industrial purposes. These pipes are frequently employed in a medium where Cl$^{-}$ ions are present [10]. In the presence of chloride ions, Cu$^{+}$ ions is converted to the soluble CuCl$_2^-$ by reacting with excess chloride [16].

At chloride concentrations lower than 1 M, the dissolution of copper occurs through formation of CuCl, which is not protective enough and is converted to the soluble CuCl$_2^-$ by reacting with excess chloride [16].

On the other hand, at concentrations higher than 1 M, higher cuprous complexes such as CuCl$_2^-$ and CuCl$_2$$_2^-$ are formed, in addition to the ones with fewer chlorides, such as CuCl and CuCl$_2$$_2$– [17].

One of the most important methods in the protection of metals against corrosion is the use of organic inhibitors, a large number of organic compounds has been reported in the last decades as corrosion inhibitors of metals [18–29]. Many organic molecules are used to inhibit copper corrosion [30–32]. Heterocyclic compounds containing nitrogen and sulphur are known to be good corrosion inhibitors of copper and alloys in various aggressive media. Benzotriazole (BTA) is one of the most important inhibitor for copper and copper alloy corrosion in the environments of the wide temperature and pH ranges. However, the most serious deficiency in BTA is its toxicity [33].

Currently, research in copper corrosion is oriented to the development of green corrosion inhibitors; compounds with good inhibitory efficiency but low or zero risk of environmental pollution [34–36].

The present work aims to characterize the effect of N-(5,6-diphenyl-4,5-dihydro-[1,2,4]triazin-3-yl)-guanidine (NTG) as a green corrosion inhibitor of Cu in 3% NaCl solution using weight loss measurements and electrochemical methods include potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM).
2. Experimental

2.1. NTG structure

Chemical structures of the studied compound are presented in Fig. 1. NTG is relatively cheap, and easy to produce in purity greater than 99%. The non-toxic and biodegradable nature of NTG makes the investigation of its inhibiting properties significant in the context of the current priority to produce "green" or "environmentally friendly" inhibitors. NTG was obtained by refluxing guanidine hydrochloride with 5,6-diphenyl-4,5-dihydro-[1,2,4]triazin-3-thiol in DMF for 2 h according to the schematic representation shown in Fig. 1.

The coupons were polished, dried and weighted (1). Then suspended in 50 ml aerated solution of 3% NaCl without and with different concentrations of NTG. All experiments were conducted at 298 K and the temperature was kept constant using thermostat.

The weight loss experiments were carried out using rectangular copper coupons from Johnson Mathey (Puratronic, 99.999%) having dimensions of length 3.0 cm, width 1.0 cm, and thickness 0.20 cm with an exposed total area of 7.6 cm². A copper rod of the same composition was mounted in Teflon with an exposed area of 0.28 cm² and used for potentiodynamic polarization, EIS and EFM, measurements. The coupons were polished, dried and weighted (m₁), and then suspended in 50 ml aerated solution of 3% NaCl without and with different concentrations of NTG for exposure period (4 days = 96 h). After the designated exposure to the test solution, the specimens were rinsed with bidistilled water, washed with acetone to remove a film possibly formed due to the inhibitor, dried between two tissue papers, and then suspended in 50 ml aerated solution of 3% NaCl with and without NTG. Weight loss measurements were made in triplicate and the loss of weight was calculated by taking an average of these values.

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The electrochemical measurements were performed in a typical three-compartment glass cell consisting of the copper specimen as working electrode (WE), platinum mesh as counter electrode (CE), and a saturated calomel electrode (SCE) as the reference electrode. The counter electrode was separated from the working electrode compartment by fritted glass. The reference electrode was connected to a Luggin capillary to minimize IR drop. Solutions were prepared from bidistilled water of the resistivity 13 MΩ cm. Prior to each experiment, the specimen was polished with a series of emery papers of different grit sizes up to 4/0 grit, polished with Al₂O₃ (0.5 mm particle size), washed several times with bidistilled water then with acetone and dried using a stream of air. The electrode potential was allowed to stabilize for 40 min before starting the measurements. The aggressive environment used was 3% NaCl solution with different concentrations of NTG. All experiments were conducted at 298 K and the temperature was kept constant using thermostat.

Potentiodynamic polarization curves were obtained by changing the electrode potential automatically from (−450 to +150 mV) versus open circuit potential with a scan rate of 1 mV s⁻¹.

EIS measurements were carried out in a frequency range of 100 kHz to 20 mHz with amplitude of 5 mV peak-to-peak using ac signals at respective corrosion potential.

EFM carried out using two frequencies 2 and 5 Hz. The base frequency was 1 Hz, so the waveform repeats after 1 s. The higher frequency must also be sufficiently slow that the charging of the double layer does not contribute to the current response. Often, 10 Hz is a reasonable limit. In this study, we use a perturbation signal with amplitude of 10 mV for both perturbation frequencies of 2 and 5 Hz. The choice for the frequencies of 2 and 5 Hz was based on three principles [37]. First, the harmonics and intermodulation frequencies should not influence each other. Second, the frequency should be as low as possible to avoid influence of the capacitive behaviour of the electrochemical double layer. Third, the frequency should be as large as possible to reduce time needed to perform a measurement. While these arguments do not allow the selection of "perfect" frequencies, the chosen frequencies were considered as reasonable compromise.

Measurements were performed with a Gamry instrument PotentioStat/Galvanostat/ZRA, this includes a Gamry framework system based on the ESA4000, Gamry applications that include DC105 for dc corrosion measurements, EIS300 for EIS measurements and EFM140 to calculate the corrosion current and the Tafel constants for EFM measurements. A computer was used for collecting data. Echem Analyst 4.0 Software was used for plotting, graphing and fitting data. The molecular dynamics (MD) simulations were performed using the commercial software MS Modelings from Accelrys. For quantum chemical calculations, the study was carried out using Dewar's linear combinations of atomic orbitals–self-consistent field–molecular orbital (LCACO–SCF–MO) [38,39], ab initio with basis set STO-3G method with commercially available quantum chemical software, HyperChem, Release 8.0 [40].

3. Results and discussion

3.1. Weight loss measurements

The spontaneous dissolution of copper in 3% NaCl solutions containing different concentrations of NTG was studied by weight loss measurements.

Fig. 2 shows corrosion rate calculated from weight loss at different concentrations of NTG, ranging from 10⁻⁴ to 10⁻² M at 298 K. Corrosion rate and inhibition efficiencies can be calculated from equations:

\[ CR = \frac{m_1 - m_2}{A \times T} \] (1)

\[ IE\% = \frac{(CR)_0 - (CR)}{(CR)_0} \times 100 \] (2)

where \( m \) is the weight loss in grams, \( A \) is the total surface area in cm², \( T \) is the time of exposure in h, and \((CR)_0\) and \((CR)\) are the corrosion rates in (mg cm⁻² h⁻¹) without and with NTG, respectively.

The corrosion parameters such as inhibition efficiency (IE%) and corrosion rate CR at different concentration of NTG in 3% NaCl at 298 K are presented in Table 1. As can be seen from Table 1, NTG inhibits the corrosion of copper at all concentrations. Data in Table 1 reveal that the inhibition efficiency increases with increasing concentration of NTG. NTG is a "biodegradable" inhibitor. NTG was obtained by refluxing guanidine hydrochloride with 5,6-diphenyl-4,5-dihydro-[1,2,4]triazin-3-thiol in DMF for 2 h according to the schematic representation shown in Fig. 1.

The weight loss experiments were carried out using rectangular copper coupons from Johnson Mathey (Puratronic, 99.999%) having dimensions of length 3.0 cm, width 1.0 cm, and thickness 0.20 cm with an exposed total area of 7.6 cm². A copper rod of the same composition was mounted in Teflon with an exposed area of 0.28 cm² and used for potentiodynamic polarization, EIS and EFM, measurements.
Table 1

<table>
<thead>
<tr>
<th>Concentration/M</th>
<th>CR/mg cm⁻² h⁻¹</th>
<th>Coverage θ</th>
<th>IE/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>162.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10⁻⁴</td>
<td>76.05</td>
<td>0.53</td>
<td>53.2</td>
</tr>
<tr>
<td>10⁻³</td>
<td>5.85</td>
<td>0.96</td>
<td>96.4</td>
</tr>
<tr>
<td>10⁻²</td>
<td>0.325</td>
<td>0.99</td>
<td>99.8</td>
</tr>
</tbody>
</table>

concentration of NTG. The corrosion inhibition can be attributed to the adsorption of NTG molecules at copper/NaCl solution interface. The inhibition efficiency depends on the degree of the surface coverage (θ) [41] of the metal surface by molecules of the inhibitor and can be expressed as

\[
\theta = \frac{(CR)_0 - (CR)}{(CR)_0}
\]

The degree of the surface coverage (θ), is evaluated from weight loss measurements using Eq. (3). Values of surface coverage (θ) for copper in 3% NaCl, in different concentrations of NTG are given in Table 1. As the concentrations of NTG increase, θ values increase and acquire the highest value of (0.99) in the solution of 10⁻² M of NTG.

3.2. Electrochemical measurements

3.2.1. Potentiodynamic polarization

Figs. 3–5 show the potentiodynamic polarization curves of copper electrodes after different immersion times at the respective corrosion potentials in 3% NaCl solutions containing different concentrations of NTG. The three distinct regions that appeared were the active dissolution region (apparent Tafel region), the active-to-passive transition region, and the limiting current region. In the absence of NTG, the anodic polarization curve of copper showed an 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 CuCl film formation. In the presence of NTG, both the cathodic and anodic current densities were greatly decreased. The corresponding electrochemical kinetics parameters, as corrosion potential (Ecorr), cathodic and anodic Tafel slopes (βa, βc) and corrosion current density (icorr), obtained by extrapolation of the Tafel lines. The inhibitor efficiency was evaluated from dc measurements using the following Equation [10]:

\[
IEp% = \left(1 - \frac{i_{corr}}{i_{corr}^0}\right) \times 100
\]

where \(i_{corr}^0\) and \(i_{corr}\) correspond to uninhibited and inhibited current densities, respectively.

According to Figs. 3–5 and Table 2, the corrosion inhibition of copper increases with different NTG concentration and immersion time at the respective corrosion potentials. For the lowest concentration of NTG (10⁻⁴ M), low inhibition is observed at short immersion times (15 min). For example, when the concentration of NTG is 10⁻⁴ M, inhibition efficiency was 37% (at 15 min immersion) it increases remarkably and reached 95% after 60 min immersion. It reached 99% at 1500 min immersion in 3% NaCl. Short immersion times brings about a negative shift of corrosion potential, Ecorr (−179 to −240 mV). However, relatively constant values of Ecorr are obtained with different concentrations of NTG after long immersion times. Table 2 clearly shows that icorr values approach a stable value after 1500 min immersion in the investigated time scale. NTG reduces both anodic and cathodic currents of copper corrosion. There is no definite shift for Ecorr, indicating that NTG acts as
mixed-type inhibitor in 3% NaCl. Values of $\beta_a$ and $\beta_c$ increases with increasing concentration of NTG. The increase in $\beta_a$ and $\beta_c$ values is related to the decrease in the cathodic and anodic currents, which in turn limits the electro-dissolution of copper.

Corrosion current density $i_{corr}$ obtained from immersion of copper electrode for 3000 min (50 h) and 6000 min (100 h) in 3% NaCl in presence of $10^{-2}$ M of NTG gave similar results to that obtained after immersion for 60 min as can be seen in Fig. 6. Therefore, the existence of 3% NaCl promotes greatly the protection of NTG.

3.2.2. Electrochemical impedance spectroscopy

The EIS provides important mechanistic and kinetic information for an electrochemical system under investigation.

Fig. 7 shows typical Nyquist impedance plots obtained for the Cu electrode at respective corrosion potentials after 60 min immersion in 3% NaCl in presence and absence of various concentrations of NTG. Symbols represent the measured data and solid lines represent the fitting data obtained using the equivalent circuit [5] inserted in Fig. 7. The parameters obtained by fitting the experimental data by using the equivalent circuit, and the calculated inhibition efficiencies are listed in Table 3, where $R_s$ represents the solution resistance, $R_p$ is the polarization resistance and can be defined also as the charge-transfer resistance, $CPE_1$ and $CPE_2$ are constant phase elements (CPEs), $R'_p$ is another polarization resistance and $W$, is the Warburg impedance. The Nyquist plots presented in Fig. 7 clearly demonstrate that the shapes of these plots for inhibited copper electrode are not substantially different from those of uninhibited electrode. Addition of NTG molecules increases the impedance but does not change other aspects of the electrode behaviour.

The impedance spectra obtained for copper in 3% NaCl contains depressed semicircle with the center under the real axis, such behaviour is characteristic for solid electrodes and often referred to as frequency dispersion and attributed to the roughness and other inhomogeneities of the solid electrode [42,43].

Parameters derived from EIS measurements and inhibition efficiency is given in Table 3. Addition of NTG increases the values of $R_p$ and $R'_p$ and lowers the values of $CPE_1$ and $CPE_2$ and this effect is seen to be increased as the concentrations of NTG increase. The constant phase elements (CPEs) with their $n$ values close to 1.0 represent double layer capacitors with some pores [5]; the CPEs decrease upon increase in NTG concentrations, which are expected to cover the charged surfaces and reducing the capacitive effects. This decrease in (CPE) results from a decrease in local dielectric constant and/or an increase in the thickness of the double layer, suggested that NTG molecules inhibit the copper corrosion by adsorption at the copper/NaCl interface The semicircles at high frequencies in Fig. 7 are generally associated with the relaxation of electrical double layer capacitors and the diameters of the high frequency semicircles can be considered as the charge-transfer resistance ($R_{ct} = R_p$) [42]. Therefore, the inhibition efficiency, IE% of NTG for the copper electrode can be calculated from the charge-
Table 3
Parameters obtained by fitting the Nyquist plots shown in Fig. 7 with the equivalent circuit inserted in Fig. 7 for copper in 3% NaCl solutions in absence and presence of various concentrations NTG

<table>
<thead>
<tr>
<th>Concentration/M</th>
<th>$R_{s}/\Omega \text{ cm}^2$</th>
<th>CPE$_1$</th>
<th>$R_p/k\Omega \text{ cm}^2$</th>
<th>CPE$_2$</th>
<th>$R'_p/k\Omega \text{ cm}^2$</th>
<th>$W$</th>
<th>IE$_i$/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>90.2</td>
<td>0.98</td>
<td>0.94</td>
<td>182</td>
<td>8.31</td>
<td>2.8</td>
<td>1.58E-5</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>93.2</td>
<td>0.51</td>
<td>0.85</td>
<td>345</td>
<td>3.91</td>
<td>0.52</td>
<td>224</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>92.3</td>
<td>0.12</td>
<td>0.86</td>
<td>3,689</td>
<td>1.03</td>
<td>0.54</td>
<td>534</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>90.5</td>
<td>0.06</td>
<td>0.78</td>
<td>22,765</td>
<td>0.29</td>
<td>0.48</td>
<td>632</td>
</tr>
</tbody>
</table>

transfer resistance as follows [42]:

$$IE_i/\% = \left(1 - \frac{R_0^p}{R_p}\right) \times 100$$

where $R_0^p$ and $R_p$ are the charge-transfer resistances in the chloride solution without and with different concentrations of NTG, respectively.

The CPEs are almost like Warburg impedance with their $n$ values close to 0.5 in all solutions [5], especially in presence of NTG, which suggests that the electron transfer reaction corresponding to the second semicircle takes place through the surface layer and limits the mass transport (Warburg). The presence of the Warburg ($W$) impedance in the circuit confirms also that the mass transport is limited by the surface passive film.

3.2.3. Electrochemical frequency modulation (EFM)

Figs. 8–11 show plots of current as a function of frequency that was obtained by FFT from the experimental current–time curve determined with EFM using Gamry software. EFM is a non-destructive corrosion measurement technique that can directly give values of the corrosion current without prior knowledge of Tafel constants. Figs. 8–11 show the current response contains not only the input frequencies, but also contains frequency components which are the sum, difference, and multiples of the two input frequencies.
The frequency spectrum of the current response in Figs. 8–11 contains components at harmonic and intermodulation frequencies. The harmonic components \( i_{2\omega_1} \) and \( i_{2\omega_2} \) are measured at angular frequencies \( 2\omega_1 \) and \( 2\omega_2 \). The intermodulation components \( i_{\omega_2+\omega_1} \) and \( i_{\omega_1+\omega_2} \) are measured at angular frequencies \( \omega_2 + \omega_1 \) and \( \omega_1 + \omega_2 \), respectively.

In EFM technique the \( i_{\text{corr}} \) values and Tafel slopes are calculated as the ratio of two or three current values that are measured at different frequencies.

The corrosion current \( i_{\text{corr}} \) and the Tafel parameters are determined according to the following Eqs. (6)–(8) [44]:

\[
i_{\text{corr}} = \frac{(i_{\omega_1 \cdot \omega_2})^2}{2\sqrt{(8i_{\omega_1 \cdot \omega_2}i_{2\omega_2+\omega_1} - 3i_{\omega_2+\omega_1})^2}}
\]

\[
\beta_a = \frac{i_{\omega_1 \cdot \omega_2}U_0}{i_{\omega_2+\omega_1} + \sqrt{(8i_{\omega_1 \cdot \omega_2}i_{2\omega_2+\omega_1} - 3i_{\omega_2+\omega_1})^2}}
\]

\[
\beta_c = \frac{i_{\omega_1 \cdot \omega_2}U_0}{-i_{\omega_2+\omega_1} + \sqrt{(8i_{\omega_1 \cdot \omega_2}i_{2\omega_2+\omega_1} - 3i_{\omega_2+\omega_1})^2}}
\]

where \( U_0 \) is the applied ac potential which is 10 mV for both perturbation frequencies of 2 and 5 Hz.

The great strength of the EFM is the Causality Factors (CF-2 and CF-3), which serve as an internal check on the validity of the EFM measurement [44].

The inhibition efficiency calculated from EFM measurements can be calculated from the following equation:

\[
\text{IEEFM}\% = \left(1 - \frac{i_{\text{corr}}}{i_{0\text{corr}}}\right) \times 100
\]

As can be seen from Table 4, the corrosion current densities decrease with increase in NTG concentrations. The causality factors in Table 4 indicate that the measured data are of good quality. The standard values for CF-2 and CF-3 are 2.0 and 3.0, respectively. The causality factor is calculated from the frequency spectrum of the current response. If the causality factors differ significantly from the theoretical values of 2.0 and 3.0, then it can be deduced that the measurements are influenced by noise. If the causality factors are approximately equal to the predicted values of 2.0 and 3.0, there is a causal relationship between the perturbation signal and the response signal. Then the data are assumed to be reliable [37]. When CF-2 and CF-3
are in the range 0–2 and 0–3, respectively, then the EFM data is valid.

In Table 4, the inhibition efficiencies $\text{IE}_{\text{EFM}}\%$ increase with increase in NTG concentrations up to 99% with addition of $10^{-2}$ M from NTG. The causality factors CF-2 and CF-3 are close to their theoretical values of 2.0 and 3.0, respectively.

### 3.3. Adsorption of NTG

Several adsorption isotherms were assessed and the Langmuir adsorption isotherm was found to be the best description of the adsorption behaviour of the studied inhibitor, which obeys the following Eqs. (10) and (11) [45]:

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{b} + C_{\text{inh}}$$  \hspace{1cm} (10)

$$b = \frac{1}{55.5} \exp \left( - \frac{\Delta G_{\text{ads}}^0}{RT} \right)$$  \hspace{1cm} (11)

$c_{\text{inh}}$ is the inhibitor concentration, $\theta$ is the fraction of the surface coverage, $b$ is the adsorption coefficient and $\Delta G_{\text{ads}}^0$ is the standard free energy of adsorption.

Fig. 12 shows the dependence of the fraction of the surface coverage $C/\theta$ as a function of the concentration ($C$) of NTG. The degree of surface coverage $\theta$ in Table 1 for different concentrations of the inhibitor in 3% NaCl has been evaluated from weight loss measurements using equation (3). The obtained plot of the inhibitor is linear. The regression coefficient is $R^2 = 0.999$. The intercept permits the calculation of the equilibrium constant $b$ which is equals 2350901.7 M$^{-1}$ and leads to evaluate $\Delta G_{\text{ads}}^0 = -46.294$ kJ mol$^{-1}$. The negative value of $\Delta G_{\text{ads}}^0$ indicates that the inhibitor is spontaneously adsorbed on the metal surface [46]. The large negative value of $\Delta G_{\text{ads}}^0$ indicated that NTG was strongly adsorbed on the copper surface [47]. It is well known that values of $\Delta G_{\text{ads}}^0$ of the order of 20 kJ mol$^{-1}$ or lower indicate a physisorption, while those of order of 40 kJ mol$^{-1}$ or higher involve charge sharing or charge-transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond [48,49]. On the other hand, Metikos-Hukovic et al. [50] describe the interaction between thiourea and iron ($\Delta G_{\text{ads}}^0 = -39$ kJ mol$^{-1}$) as chemisorption. Values of $\Delta G_{\text{ads}}^0$ proof that the adsorption of NTG on copper surface in 3% NaCl is chemisorptions in nature.

### 3.4. Quantum chemical and molecular simulation study

Computation of some key quantum chemical indices has been carried out using the PM3 method, the calculated quantum chemical indices include energy of the highest occupied molecular orbital ($E_{\text{HOMO}} = -9.1$ eV); energy of the lowest unoccupied molecular orbital ($E_{\text{LUMO}} = -0.78$ eV); dipole moment ($\mu = 6.1$ D) and the energy gap, $\Delta (E_{\text{HOMO}} - E_{\text{LUMO}}) = -8.22$ eV. These quantum chemi-
The high inhibition efficiency of NTG can be attributed to the high value of $E_{\text{HOMO}}$ and dipole moment $\mu$ and low values of $E_{\text{LUMO}}$ and $\Delta$. The results seem to indicate that the charge transfer from NTG takes place during adsorption to the copper oxide/chloride surface [10]. High values of $E_{\text{HOMO}}$ may facilitate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer.

In order to get more information on the probable centre of adsorption, molecular dynamics simulation studies were performed to simulate the adsorption structure of the NTG molecule on copper surface in presence of solvent molecules and in an attempt to understand the interactions between NTG molecule and copper surface.

Molecular structure of NTG shows that it is likely to adsorb on copper surface by sharing the electrons of nitrogen atoms with copper oxide/copper chloride, layer to form coordination bonds between Cu–N as well as π-electron interactions between the aromatic rings and copper surface. Both interactions can make it possible for NTG to form coordinate bond with copper surface. The adsorption progress of NTG on copper surface is investigated by performing molecular dynamics using Amorphous Cell module in MS Modeling software, which provides a comprehensive set of tools to perform atomic simulations on complex systems. Fig. 13 shows the amorphous cell containing the copper substrate, the solvent molecules and NTG molecule. Adsorption energy calculated for the adsorption of NTG in presence of the copper substrate and solvent molecules equals $-44$ kJ mol$^{-1}$. Inspection of Fig. 13 shows that, the adsorption centers are only N(3) and N(4) with negative charge participate to the adsorption phenomenon. On the other hand, N(1), N(2), N(5) and N(6) with positive charge do not participate at the adsorption process.

4. Conclusions

The main conclusions drawn from this study are:

- NTG inhibits the corrosion of copper in 3% NaCl solutions.
- The inhibition is due to adsorption of the inhibitor molecules on the copper surface and blocking its active sites.
- Adsorption of the inhibitor fits a Langmuir isotherm model.
- Results obtained from weight loss, dc polarization, ac impedance and EFM techniques are in reasonably good agreement and show increased inhibitor efficiency with increasing inhibitor concentration.
- Efficiency of NTG increases as the immersion time increases.
- Polarization data shows that NTG acts as mixed-type inhibitor in 3% NaCl.

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