Experimental and atomistic simulation studies of corrosion inhibition of copper by a new benzotriazole derivative in acid medium

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ABSTRACT

The efficiency of N-(2-thiazolyl)-1H-benzotriazole-1-carbothioamide (TBC) as a non-toxic corrosion inhibitor for copper in 0.5 M HCl has been tested by weight loss and electrochemical techniques. Electrochemical techniques show that TBC is a mixed-type inhibitor and its inhibition mechanism on copper surface is adsorption assisted by H-bond formation. Impedance measurements show a wide peak presumably given by more than one time constant in the presence of TBC. Also, impedance results show that the values of CPEs (constant phase elements) tend to decrease and both polarization resistance and inhibition efficiency tend to increase with increasing of TBC concentration due to an increase in the electric double layer. Monte Carlo simulations incorporating molecular mechanics and molecular dynamics show that the TBC adsorb on the copper surface firmly through the thiazolyl and carbothioamide groups, the adsorption energy as well as hydrogen bond length have been calculated for both TBC and benzotriazole (BTA) for comparison. Quantum chemical calculations reveal that TBC has higher HOMO, lower LUMO, lower energy gap and lower dipole moment (μ) than BTA, which proves that TBC is better copper corrosion inhibitor compared with BTA in 0.5 M HCl.

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1. Introduction

The behaviour of copper in acidic media is extensively investigated and several ideas have been presented for the dissolution process [1–3]. A number of investigations have also been conducted on the electrodissolution of copper in acidic media in the presence of benzotriazole (BTA) [4–8]. Benzotriazole is one of the most effective inhibitors for corrosion of copper and its alloys. As reported in the literature, in the presence of benzotriazole, the copper surface is covered by a film, which inhibits the process of electrodissolution. This film has been identified as a polymeric [Cu(I)BTA] complex by spectroscopic techniques [9,10]. For chloride media some papers in the literature have suggested a weak effect of benzotriazole in low pH below the limiting current [8,11]. However, under the same conditions a polymeric [Cu(I)BTA] complex and [Cu(I)Cl-BTAH] have been found by Raman spectroscopy [12].

To be able to reveal new and effective corrosion inhibitors for copper in 0.5 M HCl solutions, a new benzotriazole derivative namely, N-(2-thiazolyl)-1H-benzotriazole-1-carbothioamide, TBC, has been used as possible inhibitor for copper corrosion in 0.5 M HCl. The interactions between the inhibitor molecules and the metal surfaces should by all means be explained and understood in detail. In examining of these interactions, theoretical approaches can be applied very useful. Therefore, recently an increasing attention was seen on the involvement of these theoretical approaches in corrosion studies [13–21].

Molecular modeling has the potential to study this adsorption and possibly identify structurally similar compounds worthy of synthesis and subsequent corrosion testing. Thus, if a molecular mechanics model of the interactions that control the adsorption of a minimized structure with a particular metal can be set up, a measure of the binding of these molecules and the metal surface can be achieved [22].

Molecular modeling has not been used widely for inhibition studies. Bartley et al. [22] studied the docking of alky esters on copper surface computationally. Edwards et al. [23] investigated the adsorption of the oil field pipeline inhibitor, oleic imidazoline using both molecular orbital and molecular mechanics methods, Fitzwater [24] employed molecular mechanics and molecular dynamics to simulate the adsorption of both poly acrylic acid and poly aspartic acid on various CaCO3 surfaces. Khaled [25] studied the adsorption behaviour of some triazole derivatives using molecular simulations, quantum chemical calculations and electrochemical studies and found that molecular modeling techniques incorporating molecular mechanics and molecular dynamics can be used to simulate the adsorption of these inhibitors on iron surface.

On continuation of our work on using molecular modeling techniques incorporating molecular mechanics and molecular
dynamics [25], the present work aims to study the in situ a uence of TBC on the inhibition of pure copper corrosion in 0.5 M HCl solutions using chemical (weight loss), electrochemical techniques (potentiodynamic polarization and electrochemical impedance spectroscopy) as well as explicit solvent simulations using molecular dynamics and quantum chemical calculation to explore the adsorption mechanism of TBC on copper surface (1 1 0).

2. Experimental

2.1. Chemical and electrochemical measurements

Chemical structure of the studied compound is presented in Fig. 1. Copper specimens from Johnson Mathey (Puratronic, 99.999%) were mounted in Teflon. An epoxy resin was used to fill the space between Te on and copper electrode. The circular cross-sectional area of the copper rod exposed to the corrosive medium that used in electrochemical measurements was 0.28 cm². Weight loss measurements carried out using copper rods of the same composition, each of size 2 cm length and 0.5 cm diameter (surface area = 6.5 cm²). The electrochemical measurements were performed in a typical three-compartment glass cell consisted of the copper specimen as working electrode (WE), platinum 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 resistivity 13 MΩ cm, the copper electrode was polished with different grit emery papers up to 4/0 grade, cleaned with acetone, washed with bidistilled water and finally dried.

The electrode potential was allowed to stabilize for 30 min before starting the measurements. All experiments were conducted at 30 ± 1°C. The electrolyte solution was made from HCl (Fisher Scientific) and bidistilled water. The inhibitors (Aldrich Chemical Co.) used without any pretreatment. Measurements were performed using Gamry Instrument Potentiostat/Galvanostat/ZRA. This includes a Gamry Framework system based on the ESA400, Gamry applications that include dc105 for dc corrosion measurements, EIS300 for electrochemical impedance spectroscopy measurements along with a computer for collecting data. Echem Analyst 4.0 Software was used for plotting, graphing and fitting data.

The potentiodynamic current–potential curves were obtained by changing the electrode potential automatically from (−800 to +200 mV SCE) at open circuit potential with a scan rate of 0.1 mV s⁻¹. EIS measurements were carried out in frequency range from 100 kHz to 10 mHz with an amplitude of 5 mV peak-to-peak using ac signals at open circuit potential. EIS spectra were analyzed by Zview impedance analysis software (Scribner Associates Inc., Southern Pines, NC).

2.2. Computational details

Molecular simulation studies were performed using Materials studio 4.3 software from Accelrys Inc. [26] which has been used to build TBC molecules, copper (1 1 0) surface and solvent molecules using the sketching tools in Materials Visualizer. Also, the periodic structures can be built using the tools available in the Materials Visualizer for building crystals and surfaces. Molecular mechanics tools are used to investigate the copper/solvent/TBC system. The key approximation is that the potential energy surface, on which the atomic nuclei move, is represented by a classical forcefield. Forcefield is developed by parameterizing data from experiment and high level quantum mechanical calculations. COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) [27] which used to optimize the structures of all components of the system of interest (copper/solvent/TBC) represents a technology break-through in forcefield method. It is the first ab initio forcefield that enables accurate and simultaneous prediction of chemical properties (structural, conformational, vibrational, etc.) and condensed-phase properties (equation of state, cohesive energies, etc.) for a broad range of chemical systems. It is also, the first high quality forcefield to consolidate parameters of organic and inorganic materials.

The first step in this computational study is the preparation of a model of molecules which will adsorb on the surface with optimized geometry (i.e. energy minimized). Among the different steps involved in the modeling approach is the construction of the copper surface from its pure crystal, the addition of the TBC molecule near to the surface, the definition of the potentials (i.e. the forcefield) to study the liquid–solid interaction, followed by the geometry optimization calculation. The same procedure is carried out with BTA for comparison. This particular case, the use of molecular mechanics can be seen as a precursor to computationally more expensive quantum chemical methods: once the model has been optimized with suitable forcefield (COMPASS), we will be able to simulate a substrate (copper surface) loaded with an adsorbate (TBC or BTA) taking into consideration the solvent effect. This computational study aims to find low energy adsorption sites to investigate the preferential adsorption of TBC or BTA on copper surface aiming to find a relation between the effect of their molecular structure and their inhibition efficiency.

To build copper surface, amorphous cell module has been used to create solvent/TBC cell on copper surface. The behaviour of TBC and BTA on the surface was studied using molecular dynamics simulations and the COMPASS forcefield. The MD simulation of the interaction between the TBC molecule dissolved in H₂O and the copper surface (1 1 0) was carried out in a simulation box (29.97 Å × 29.97 Å × 29.96 Å) with periodic boundary conditions in order to simulate a representative part of an interface devoid of any arbitrary boundary effects. A cutoff distance of 1.0 nm with a spline switching function was applied for the non-bond interactions, i.e., for coulombic, van der Waals and hydrogen bond interactions. The cutoff used to select the spline width which specifies the size of the region within which non-bond interactions are splined from their full value to zero. For the actual computation of this interaction energy, charge groups are used. The copper crystal is cleaved along with the (1 1 0) plane, thus representing the copper surface. For the MD simulation, all the spatial positions of the copper atoms in the simulation box are fixed because the thermal vibrations of the interaction with an adsorbed molecule and not in the physical behaviour of the crystal itself. The liquid phase consists of 400 H₂O molecules and a single dissolved inhibitor molecule. On the top of this “a eous layer , an additional layer of 200 H₂O molecules with fixed spatial positions serves as an upper limit for the liquid phase acting like a wall but with the same physical and chemical properties. The MD simulation simulates a substrate loaded with an adso-
bate (one molecule of TBC or BTA). A low energy adsorption site is identified by carrying out a Monte Carlo search of the conformational space of the substrate–adsorbate system as the temperature is slowly decreased.

The Monte Carlo docking procedure is based on the random selection of positions and orientations of a molecule above the surface, followed by calculation of the trial interaction energy for the copper–TBC system. If this energy is below threshold value (chosen to exclude excessive steric contact) the docked conformation is accepted, and saved for further investigation. If the energy is higher than the threshold value a random choice of position and orientation is made again, and the energy evaluation is repeated. All structures used in this study are minimized in order to ensure that the energy results used in calculating the adsorption energy of TBC molecule. This includes not only the forcefield, atomic charges, and non-bond summation methods, but also the quality of the energy and geometry optimization calculations and the convergence tolerances used for the minimization.

For the quantum chemical calculations, the study was carried out using Dewar’s linear combinations of atomic orbitals–self-consistent field–molecular orbital (LCAO–SCF–MO) [28]. We used PM3 semi-empirical method in commercially available quantum chemical software Hyperchem, release 8.06 [29]. A full optimization of all geometrical variables without any symmetry constraint was performed at the restricted Hartree–Fock (RHF) level. It develops the molecular orbitals on a valence basis set and also calculates electronic properties and optimized geometries of both TBC and BTA molecules. As an optimization procedure, the built-in Polak-Ribiere algorithm was used [30].

3. Results and discussion

3.1. Weight-loss measurements

Table 1 shows corrosion rate (C.R.) of copper and inhibition efficiency $I_{w\%}$ by weight-loss measurements at different inhibitor concentrations in 0.5 M HCl at 30 ± 1 °C. The inhibition efficiencies $I_{w\%}$ were calculated using the following equation:

$$I_{w\%} = \left(1 - \frac{w_{o}}{w_{a}}\right) \times 100$$  \hspace{1cm} (1)


where $w_{o}$ and $w_{a}$ are rates of corrosion (mg cm$^{-2}$ h$^{-1}$) without and with TBC, respectively.

Table 1 shows that inhibitor efficiency increases with increase in inhibitor concentration. For this purpose, one observes that the optimum concentration of inhibitor required to achieve the maximum efficiency is found to be $5 \times 10^{-2}$ M ($I_{w\%} = 96.36$).

![Fig. 2. Anodic and cathodic polarization curves for copper in 0.5 M HCl solutions in the absence and presence of various concentrations of TBC at 30 °C.](image)

3.2. Potentiodynamic polarization measurements

Fig. 2 shows cathodic and anodic polarization curves recorded for Cu in 0.5 M HCl solutions in the absence and presence of various concentrations of TBC. Anodic curves in Fig. 2 can be divided into three regions: (1) the apparent-Tafel region, associated with the formation of CuCl$_2^-$, is observed at relatively low current densities; (2) the limiting-current region, associated with the formation of a CuCl film, is observed at higher current densities; and (3) the region beyond the limiting-current plateau, in which the current density increases due to the formation of Cu$^2+$. Lee and Nobe [31] reported the occurrence of a current peak between the apparent-Tafel and limiting-current regions during potential sweep experiments. The electrode dissolution of copper in the apparent-Tafel region has been found to follow Tafel-like behaviour, with a slope of 60 mV/decade, and the reaction is controlled by both mass-transfer and activation processes [32]. In this study where the chloride ion concentration is 0.5 M, the rate of corrosion reaction is proportional to [Cl$^-]^2$, reflecting the formation of CuCl$_2^-$, while at higher concentrations the reaction is proportional to [Cl$^-]^x$ where $x > 2$ [33]. The electrode-solution of Cu in 0.5 M HCl solutions may be expressed in terms of the following mechanism. The initial step is the electroadsorption of Cl$^-$ by the reaction:

$$\text{Cu} + \text{Cl}^- \rightleftharpoons \text{CuCl}_{\text{ads}} + \text{e}^-$$  \hspace{1cm} (2)

CuCl$_{\text{ads}}$ represents a cuprous chloride species which is adsorbed onto the copper electrode surface. The rate of the electrochemical reaction (2) is given by

$$\frac{i_1}{F} = k_1C_1(0)(1 - \theta) - k_{-1}\theta$$  \hspace{1cm} (3)

where $\theta$ is the surface coverage of the CuCl$_{\text{ads}}$ adsorbed intermediate and $C_1(0)$ is the concentration of Cl$^-$ at the Cu surface. The electrochemical rate constants $k_1$ and $k_{-1}$, are dependent on the potential. The first term on the right-hand side represents the anodic term, while the second term is the cathodic term.

Fig. 2 shows that, in the inhibitor free solution an exponentially increasing Cu dissolution current is observed in the anodic scan at potentials positive of ~200 mV followed by a decrease in current above ~80 mV and a second increase above ~47 mV. Similar behaviour has been found previously by Tromans and Sun [8]. The decrease in current between ~80 and ~47 mV was attributed to the formation of CuCl film arising from the lateral growth and thickening of CuCl nuclei [34]. The anodic curve in the absence of inhibitor
is characterized by quasi-Tafelian behaviour, i.e. the anodic copper dissolution is not solely activation-controlled, but is under diffusion of soluble CuCl\(_2\) species from outer Helmholtz plane into the bulk solution [35,36]. Referring to the cathodic process, the cathodic polarization curve displayed a current plateau from \(-350\) to \(-610\) mV, which may be attributed to the diffusion-controlled reduction of oxygen. The cathodic corrosion reaction in an aerated HCl solution is

\[
4\text{H}^+ + \text{O}_2 + 4e^- \rightarrow 2\text{H}_2\text{O}
\] (4)

Also, Fig. 2 shows cathodic and anodic polarization curves for Cu in the presence of inhibitor. It is clear that the addition of inhibitor affects both the anodic and cathodic reactions, therefore the inhibitor acts as a mixed-type inhibitor. Also, no definite shift in corrosion potential was observed in Fig. 2 which confirms that the inhibitor acts as a mixed-type inhibitor. Moreover, we remark that the effect of TBC on both anodic and cathodic branches is pronounced which is a further enhancement of the corrosion inhibition effect of TBC on both anodic and cathodic branches is pronounced which is a further enhancement of the corrosion inhibition.

The slope of the anodic Tafel lines \(\beta_a\) remain almost unchanged; indicating that the presence of inhibitor in the solution has no effect on the dissolution mechanism of copper, but the inhibitor molecules blocks the active corrosion sites on the copper surface.

3.3. Electrochemical impedance spectroscopy measurements, EIS

To get further information concerning the inhibition process and to confirm the potentiodynamic polarization experiments, electrochemical impedance spectroscopic investigations of Cu in inhibitor-free and inhibitor containing 0.5 M HCl are used. EIS is a powerful tool in the investigation of the corrosion and adsorption phenomena [37]. The mechanism used in the literature to explain copper electrodissolution in HCl medium, at low current densities, presents an impedance structure with a coupling between adsorption and mass transport [38]. According to Crundwell [33] and Diard et al. [38], the mechanism of dissolution of copper in HCl solution is

\[
\begin{align*}
\text{Cu} + \text{Cl}^- & \rightarrow \text{CuCl}_{ads} + e^- \\
\text{CuCl}_{ads} + \text{Cl}^- & \rightarrow \text{CuCl}_2
\end{align*}
\] (6)

(7)

The high frequency loop is attributed to the charge transfer resistance and the double layer capacitance Eq. (6). The low frequency loop is attributed to convective and diffusion mass transport of CuCl\(_2\) from surface Eq. (7) [38]. Figs. 3–5 present the impedance diagrams for the same experimental data in Bode (\(\log Z \text{ vs. } \log f\)) and Bode-phase format (\(\log f \text{ vs. } \text{phase}\)) in the presence of different concentrations of inhibitor solutions. From the Bode plots (Fig. 4), there is no distinct diversification of impedance modulus, and the impedance modulus increase with inhibitor concentration. Fig. 5 shows the continuous increase in the phase angle shift.

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>(i_{corr} (\mu\text{Acm}^{-2}))</th>
<th>(E_{corr} (\text{mV}))</th>
<th>(\beta_a (\text{mVdec}^{-1}))</th>
<th>(\beta_c (\text{mVdec}^{-1}))</th>
<th>CR (mpy)</th>
<th>(E_p (%))</th>
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</thead>
<tbody>
<tr>
<td>Blank</td>
<td>11.62</td>
<td>288.1</td>
<td>381.7</td>
<td>60.41</td>
<td>5.33</td>
<td>-</td>
</tr>
<tr>
<td>(10^{-5})</td>
<td>6.318</td>
<td>274.2</td>
<td>570.6</td>
<td>66.0</td>
<td>2.89</td>
<td>45.63</td>
</tr>
<tr>
<td>(10^{-4})</td>
<td>4.899</td>
<td>278.2</td>
<td>546.0</td>
<td>64.89</td>
<td>2.24</td>
<td>57.84</td>
</tr>
<tr>
<td>(5 \times 10^{-4})</td>
<td>3.535</td>
<td>264.4</td>
<td>516.4</td>
<td>66.11</td>
<td>1.62</td>
<td>69.57</td>
</tr>
<tr>
<td>(10^{-3})</td>
<td>2.93</td>
<td>269.3</td>
<td>363.7</td>
<td>65.47</td>
<td>1.34</td>
<td>74.78</td>
</tr>
<tr>
<td>(5 \times 10^{-3})</td>
<td>2.202</td>
<td>278.6</td>
<td>533.5</td>
<td>64.87</td>
<td>1.01</td>
<td>81.05</td>
</tr>
<tr>
<td>(10^{-2})</td>
<td>1.389</td>
<td>277.2</td>
<td>506.1</td>
<td>65.58</td>
<td>0.64</td>
<td>88.04</td>
</tr>
<tr>
<td>(5 \times 10^{-2})</td>
<td>0.706</td>
<td>264.1</td>
<td>524.2</td>
<td>66.00</td>
<td>0.32</td>
<td>93.92</td>
</tr>
</tbody>
</table>
correlating with the increase of inhibitor adsorbed on Cu surface. The impedance spectra obtained on Cu in 0.5 M HCl consists of depressed capacitive loops. When Nyquist plot (Fig. 3) contains "depressed semicircles with the center under the real axis", such behaviour is characteristic for solid electrodes. Dispersion has been attributed to roughness and other inhomogeneities of the solid surface [39]. In these cases, the parallel network charge transfer-resistance-double layer capacitance ($R_\text{ct} - C_\text{dl}$) is usually a poor approximation especially for systems where an efficient inhibitor is present. For the description of a frequency independent phase shift between an applied ac potential and its current response, a constant phase element (CPE) is used. It is evident that phase plots (Fig. 4) show a wide peak presumably given by more than one time constant in the presence of TBC. For analysis of the impedance spectra the equivalent circuit (EC) given in Fig. 6 was used. Table 3 shows the corresponding fitted results where $R_s$ is the solution resistance, $R_1$ is the charge transfer resistance, $CPE_1$ is the capacitance of the double layer, $R_2$ and $CPE_2$ are associated with the adsorbed CuCl layer [38]. The data were fitted using constant phase element, CPE which is defined in impedance representation as

$$Z(\omega) = \frac{Z_0(j\omega)^{-n}}{}$$  \hspace{1cm} (8)

where $Z_0$ is the CPE constant, $\omega$ is the angular frequency (rad/s), $j^2 = -1$, $i$ is the imaginary number and $n$ is the CPE exponent.

It is seen from Table 3 that the value of the charge transfer resistance $R_1$ increases with the inhibitor concentration. This result is related to the corrosion protection effect of the molecules. The value of the proportional factor CPE, varies regularly as well. Two dimensions of CPE are presented, too (including that of the capacitance, i.e. F/cm$^2$), which provides a comparison, i.e. a tendency toward a decrease is observed with increasing concentration, suggesting that the TBC molecules function by adsorption at the copper solution/interface. The value of $n$ changes as well (0.65–0.91), when compared to that obtained in pure HCl. This can be attributed to a certain decrease of the initial surface inhomogeneity resulting from the inhibitor’s adsorption on the most active centers [40].

The percent inhibition efficiency is calculated by charge transfer resistance obtained from Nyquist plots, according to the following equation:

$$I_i = \frac{1 - \frac{R^2_1}{R^2_1}}{100}$$  \hspace{1cm} (9)

where $R^2_0$ and $R_1$ are the charge transfer resistance values without and with TBC, respectively. Percentage inhibition values for the TBC on copper are also, listed in Table 3. We remark that the value of inhibition efficiency increases with increase in TBC concentration up to $5 \times 10^{-2}$ M reaching a maximum value at 97%. It can be concluded that the inhibition efficiency calculated from polarization curves and electrochemical impedance spectroscopy measurements are in good agreement.

### 3.4. Computational study

#### 3.4.1. Molecular dynamics simulation

Monte Carlo simulation, molecular dynamics were performed on a system comprising a TBC molecule, solvent molecules and copper surface. TBC is placed on the surface, optimize and then run quench molecular dynamics. Fig. 7 shows the optimization energy curves for the studied molecules, before putting them on the copper surface. As it can be seen from Fig. 7 that TBC has lower optimization energy than BTA which suggest the stability of this molecule when adsorbed on copper surface compared with BTA. Total energy, average total energy, van der Waals energy, electrostatic energy and intramolecular energy for TBC/solvent/copper surface are presented in Fig. 8. Monte Carlo docking was done on each of the 100 conformations, and each of the docked structures was energetically relaxed.

The Monte Carlo simulation process tries to find the lowest energy for the whole system. The structures of the adsorbate components (TBC) are minimized until they satisfy certain specified criteria.

### Table 3

<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>$CPE_1$ (μF cm$^{-2}$)</th>
<th>$n_1$</th>
<th>$R_1$ (kΩ cm$^2$)</th>
<th>$CPE_2$ (μF cm$^{-2}$)</th>
<th>$n_2$</th>
<th>$R_2$ (kΩ cm$^2$)</th>
<th>$I_i$ (%)</th>
</tr>
</thead>
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<tr>
<td>Blank</td>
<td>4.1</td>
<td>0.85</td>
<td>0.65</td>
<td>10.22</td>
<td>9.7</td>
<td>0.92</td>
<td>1.01</td>
<td>–</td>
</tr>
<tr>
<td>10$^{-5}$</td>
<td>3.98</td>
<td>0.75</td>
<td>0.71</td>
<td>21.43</td>
<td>8.6</td>
<td>0.94</td>
<td>3.9</td>
<td>52.3</td>
</tr>
<tr>
<td>10$^{-4}$</td>
<td>6.2</td>
<td>0.63</td>
<td>0.81</td>
<td>27.12</td>
<td>7.8</td>
<td>0.89</td>
<td>5.8</td>
<td>62.36</td>
</tr>
<tr>
<td>5 $\times$ 10$^{-4}$</td>
<td>6.8</td>
<td>0.54</td>
<td>0.83</td>
<td>38.06</td>
<td>6.9</td>
<td>0.93</td>
<td>6.1</td>
<td>73.1</td>
</tr>
<tr>
<td>10$^{-3}$</td>
<td>5.9</td>
<td>0.32</td>
<td>0.79</td>
<td>49.85</td>
<td>4.8</td>
<td>0.79</td>
<td>8.3</td>
<td>79.4</td>
</tr>
<tr>
<td>5 $\times$ 10$^{-3}$</td>
<td>8.7</td>
<td>0.21</td>
<td>0.69</td>
<td>65.1</td>
<td>3.9</td>
<td>0.85</td>
<td>9.5</td>
<td>84.3</td>
</tr>
<tr>
<td>10$^{-2}$</td>
<td>8.9</td>
<td>0.11</td>
<td>0.83</td>
<td>119.5</td>
<td>2.1</td>
<td>0.93</td>
<td>12.2</td>
<td>91.4</td>
</tr>
<tr>
<td>5 $\times$ 10$^{-2}$</td>
<td>7.5</td>
<td>0.05</td>
<td>0.91</td>
<td>341.8</td>
<td>0.24</td>
<td>0.91</td>
<td>15.2</td>
<td>97.0</td>
</tr>
</tbody>
</table>

The Monte Carlo simulation process tries to find the lowest energy for the whole system. The structures of the adsorbate components (TBC) are minimized until they satisfy certain specified criteria.
The outputs and descriptors calculated by the Monte Carlo simulation are presented in Table 4. The parameters presented in Table 4 include total energy, in kcal mol$^{-1}$, of the substrate–adsorbate configuration. The total energy is defined as the sum of the energies of the adsorbate components, the rigid adsorption energy, and the deformation energy. In this study, the substrate energy (copper surface) is taken as zero. Also, adsorption energy in kcal mol$^{-1}$, reports energy released (or required) when the relaxed adsorbate components are adsorbed on the substrate. The adsorption energy is defined as the sum of the rigid adsorption energy and the deformation energy for the adsorbate components. The rigid adsorption energy, reports the energy, in kcal mol$^{-1}$, released (or required) when the unrelaxed adsorbate components (i.e., before the geometry optimization step) are adsorbed on the substrate. The deformation energy, reports the energy, in kcal mol$^{-1}$, released when the adsorbed adsorbate components are relaxed on the substrate surface. Table 4 shows also $(dE_{ads}/dT)$, which reports the energy, in kcal mol$^{-1}$, of substrate–adsorbate configurations where one of the adsorbate components has been removed. As can be seen from Table 4, TBC gives the maximum adsorption energy found during the simulation process comparing to BTA. High values of adsorption energy indicate that TBC molecule will give the highest inhibition efficiency. The close contacts between TBC, BTA and copper surface as well as the best adsorption configuration for the studied compounds are shown in Fig. 9.

### 3.4.2. Quantum chemical calculations

The effect of the molecular structure on the chemical reactivity has been subject of great interest in several disciplines of chemistry. Quantum chemical calculations have been widely used to study the reaction mechanisms and to interpret the experimental results. The calculated hydrogen bond for TBC and BTA are shown in Table 4.

### Table 4

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Total energy (kcal mol$^{-1}$)</th>
<th>Adsorption energy (kcal mol$^{-1}$)</th>
<th>Rigid adsorption energy (kcal mol$^{-1}$)</th>
<th>Deformation energy (kcal mol$^{-1}$)</th>
<th>$(dE_{ads}/dT)$ (kcal mol$^{-1}$)</th>
<th>Calculated hydrogen bond (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBC</td>
<td>-4.235</td>
<td>-80.01</td>
<td>-80.46</td>
<td>0.462</td>
<td>-80.01</td>
<td>1.57</td>
</tr>
<tr>
<td>BTA</td>
<td>-0.214</td>
<td>-75.98</td>
<td>-76.66</td>
<td>0.682</td>
<td>-75.98</td>
<td>1.82</td>
</tr>
</tbody>
</table>

Fig. 7. Optimization energy curves for TBC and BTA before putting them on the copper surface.

Fig. 8. Total energy distribution for TBC/solvent/copper system during energy optimization process.

Fig. 9. The most suitable modes of adsorption of the TBC and BTA on copper (1 1 0) showing side and top views for TBC and BTA obtained from Monte Carlo simulation process.
as well as to solve chemical ambiguities. This is a useful approach to investigate the reaction mechanisms of the inhibitor molecule and the metal surface. The structural and electronic parameters of the inhibitor molecules can be obtained by means of theoretical calculations using the computational methodologies of quantum chemistry [41]. The geometry of the inhibitor in its ground state, as well as the nature of their molecular orbitals, HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) are involved in the properties of activity of inhibitors.

$E_{\text{HOMO}}$ is a measure of electron donating ability of TBC and explains the adsorption on copper surfaces by way of delocalized lone pair of electrons. A high $E_{\text{HOMO}}$ value expresses intrinsic electron donating tendency to an appropriate acceptor, i.e. any molecule with lower $E_{\text{HOMO}}$ energy and empty molecular orbital while $E_{\text{LUMO}}$, the energy of the lowest unoccupied molecular orbital signifies the electron receiving tendency of a molecule. Accordingly, the difference between $E_{\text{LUMO}}$ and $E_{\text{HOMO}}$ energy levels, the dipole moment ($\mu$) and the electron charge on heteroatoms $(Q_N$ and $Q_S$) were determined. Based on these parameters, the calculated difference ($\Delta = E_{\text{LUMO}} - E_{\text{HOMO}}$) demonstrates inherent electron donating ability and measures the interaction of the inhibitor molecule with the copper surface. Fig. 10 shows structure of TBC as well as BTA, molecular orbital plots and the charge density distribution. It is worth noting that the charge density distribution on TBC is more delocalized than BTA which enhance the possibility of TBC to adsorb more strongly on copper surface than BTA. It is confirmed that the more negative the atomic charges of the adsorbed centre, the more easily the atom donates its electrons to the unoccupied orbital of metal [42]. So these negative atomic charges indicated that nitrogen, and sulphur atoms are the possible active adsorption sites. A hard molecule has a large energy gap, and a soft molecule has a small energy gap. Soft molecules are more reactive than hard molecules, in general. Moreover, the gap between the LUMO and HOMO energy levels of the molecules is another important factor that should be considered. Excellent corrosion inhibitors are usually those organic compounds that are not only offer electrons to unoccupied orbital of the metal surface but also accept free electrons from the metal [43,44]. The energy gap between LUMO and HOMO indicates that the smaller energy gap results in a high corrosion inhibition implying soft–soft interaction. It is well established in the literature that the higher the HOMO energy of the inhibitor, the greater the tendency of offering electrons to unoccupied d orbital of the metal, and the higher the corrosion inhibition efficiency. In addition, the lower the LUMO energy, the easier the acceptance of electrons from metal surface, as the LUMO–HOMO energy gap decreased and the efficiency of inhibitor improved. Quantum chemical parameters listed in Table 5 reveal that TBC has higher HOMO and lower LUMO than BTA. Also, Table 5 shows that, for high inhibition efficiency, the dipole moment ($\mu$) of the TBC molecules is lower than BTA, which proves that TBC is better copper corrosion inhibitor than BTA in 0.5 M HCl.

3.5. Inhibition mechanism

The adsorption of organic compounds can be described by two main types of interactions: physical adsorption and chemisorption. In general, physical adsorption requires the presence of both the electrically charged surface of the metal and charged species in solution. The surface charge of the metal is due to the electric field existing at the metal/solution interface. A chemisorption process, on the other hand, involves charge sharing or charge transfer from the inhibitor molecules to the metal surface to form a coordinate type of a bond. This is possible in case of a positive as well as a negative charge of the surface. The presence of a transition metal, having vacant, low-energy electron orbitals (Cu$^+$ and Cu$^{2+}$ in our case) and an inhibitor with molecules having relatively loosely bound electrons or heteroatoms with a lone pair of electrons is necessary for the inhibiting action [45]. Generally, two types of mechanisms of inhibition were proposed. One was the formation of polymeric complexes with copper ions (Cu$^+$ and Cu$^{2+}$) depending on the applied conditions [9,46,47]. The other was the chemical adsorption of BTA on copper surfaces [48,49]. Some studies suggested that the film formation and chemical adsorption co-exist, but the dominant mechanism depends on solution pH and applied potentials [50]. It was also, reported that the presence of benzoatri-
azole derivatives induced the formation of semiconductive copper oxides [51]. This was possibly responsible for the improvement of corrosion resistance. Research on new inhibitors or improvement of the inhibition efficiency of BTA for copper in acid has been carried out. The presence of thiazolyl group as well as carbothiomide group intermediates. This type of adsorption should be more prevalent for TBC and BTA. These results indicate that the S atom of TBC is more reactive for electrophilic attack than nitrogen atoms[52] in both TBC and BTA. These results indicate that the S atom of TBC is involved in the chemical reactivity of this molecule with the copper surface more than N atoms[53]. Therefore, TBC has the strongest interaction with copper and has better inhibitory effect on corrosion of copper in acid chloride solution than BTA.

4. Conclusions

The TBC compound is effective inhibitor for copper in 0.5 M HCl solutions. The inhibition is due to adsorption of the inhibitor molecules on the copper surface and blocking its active sites. Results obtained from dc polarization, ac impedance and weight loss techniques are in reasonably good agreement and show increased inhibitor efficiency with increasing inhibitor concentration. Molecular modeling as well as quantum chemical calculations shows that the inhibitory effect of TBC is mainly attributed to mixed adsorption mechanism assisted by H-bond formation with the copper surface.

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