Application of Electrochemical Noise to Investigate Corrosion Inhibition Properties of Some Azole Compounds on Aluminum in 0.25 M HCl

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ABSTRACT
The corrosion inhibition properties of the benzothiazole and benzotriazole inhibitors on the aluminum in 0.25 M HCl solution were studied. Electrochemical impedance spectroscopy, electrochemical noise and potentiodynamic polarization techniques were used to investigate inhibition properties of the inhibitors. Scanning electron microscope was also utilized in order to investigate the surface morphology of the samples. Results showed that benzotriazole and benzothiazole significantly reduced the corrosion rate of the aluminum. A higher corrosion inhibition efficiency of the benzotriazole compared with benzothiazole was obtained. It was shown that electrochemical noise is an appropriate technique for studying the corrosion inhibition properties of the corrosion inhibitors. Prog. Color Colorants Coat. 8(2015), 69-86 © Institute for Color Science and Technology.

1. Introduction
Aluminum as the most consuming non-ferrous metal with excellent properties like lightness, thermal and electrical conductivity has usage in wide range of applications from home appliances to aerospace industry [1-4]. The amazingly fast reaction of aluminum with its overwhelming atmosphere and formation of a passive layer on the surface could protect the aluminum from corrosion and further destruction. But this layer cannot be formed in highly corrosive media like acidic solutions which could limit the application of the aluminum for some industries [5-7]. Although the corrosion cannot be completely prevented, there are approaches to slow down the process; cathodic and anodic protection, organic and inorganic coatings, and corrosion inhibitors are the most famous ones. Among all these methods, the corrosion inhibitors especially organic inhibitors are popular choices for many applications and...
environments [8-17]. For a long time, scientists tried to characterize the interaction among metal, inhibitor and solution which lead to corrosion inhibition by organic inhibitors. Most of them concluded that adsorption of the organic inhibitor molecules instead of water molecules on the surface of metals and formation of a protective layer is the dominant mechanism. Existences of π bonds or hetero-atoms (e.g. O, N, S, and P) in the chemical structure of the organic inhibitors are believed to be responsible for their inhibition properties. It has been found that most of the corrosion inhibitors are heavily toxic and environmentally hazardous materials. However, they have been widely used due to their high corrosion inhibition properties [18-24]. In the matter of aluminum and organic inhibitors, Safak et al. [25] studied the corrosion inhibition properties of some Schiff based corrosion inhibitors on the aluminum in HCl solution. They found that the Schiff based corrosion inhibitors could reduce the corrosion of aluminum significantly. Fares et al. [26] studied the inhibition properties of the Pectin as a green inhibitor on the aluminum in HCl solution. A corrosion inhibition efficiency of 91% was obtained in the presence of Pectin on the aluminum in HCl solution.

The adsorption of azole derivatives on the iron, copper and aluminum surface has been studied by Kovacevic and Kokalj [27] by density functional theory (DFT). They showed that the role of metal d-states on the molecule surface bonding would be really important for the reactive transition metals with open d-band. The azole derivatives can be adsorbed on the Fe surface either parallel (through pronounced π-d hybridization) or vertical (through sigma bond) to the surface. The high density of "d" state around the Fermi level of the energy could be responsible for this matter. However, unlike Fe, aluminum does not have open d-band for reaction with inhibitors through π-d hybridization. The density of states (DOS) for the aluminum in the vicinity of Fermi energy consists of a very broad and flat sp-band. Due to the lower energy of "sp" band compared to "d" state in the vicinity of Fermi energy, the chemical adsorption of the inhibitors on the aluminum surface is lower than the iron. In fact, benzotriazole (BT) and benzothiazole (BTH) have large dipole moments which could interact with the metal surface by forming electrostatic dipole interactions. Naderi et al. [28] investigated the corrosion inhibition of BT and BTH on the stainless steel in acidic media. They found that BTH showed higher inhibition efficiency that BT in 1 M HCl solution on the stainless steel.

To the best of our knowledge, there is no systematic work on studying the inhibitory effects of the BT and BTH on the aluminium in HCl solution. BT has acidic hydrogen (s) and unsaturated heteroatoms (N). However, BTH has two unsaturated heteroatoms of N and S. Therefore, they can be presented in different forms of neutral, deprotonated and protonated. Depending on the form of the inhibitors, the inhibitors molecules may orient on the aluminium surface in different manners. In this study, we will investigate the differences between the inhibition action of these two azole derivatives.

Electrochemical impedance spectroscopy (EIS) and linear polarization are two well-known methods for the corrosion studies [29]. Electrochemical noise (EN) as a novel technique with numerous advantages has drawn a lot of attention in the past few years and many researchers have tried to utilize this method for different applications. EN occurs naturally in the metal/solution interface due to all procedures involved in corrosion phenomena (migration of electroactive particles, cathodic and anodic reactions, pitting initiation, etc) and the fluctuations in the potential and current generated spontaneously by the process is recorded. Since in this method there is no need to apply external perturbation, it can be completely distinctive from conventional linear polarization and EIS methods [29, 30].

Through the beneficial application of the electrochemical noise measurements we aim to compare the inhibition properties of these two well-known organic inhibitors on the aluminum in 0.25M HCl solution. Furthermore, this paper tries to compare the results obtained from various electrochemical techniques.

2. Experimental

2.1. Material and sample preparation

The corrosion inhibition properties of the BT and BTH were studied on an aluminum alloy in 0.25 M HCl solution. To this end, an aluminum alloy with chemical composition given in Table 1 was utilized. The surface of the aluminum specimens was grinded by emery papers with grit size 80 to 1200.
The grinded samples were then rinsed in distilled water and dried in air, followed by degreasing with acetone. It has been aimed to compare the corrosion inhibition properties of BTH (C_7H_5NS) and BT (C_6H_5N_3) on the aluminum surface in 0.25 M HCl solution at different concentrations. The inhibitors were used in a wide range of concentrations (25 to 1000 ppm). The chemical structures of the inhibitors are shown in Figure 1. The corrosion inhibitors and HCl solution were supplied from Merck (Germany).

2.2. Techniques

2.2.1. Scanning electron microscope (SEM)
SEM was used in order to investigate the surface morphology of the samples before and after exposure to HCl solution in the presence and absence of corrosion inhibitors. The test was carried out by a Philips model SEM at different magnifications.

2.2.2. Potentiodynamic DC polarization
The corrosion inhibition properties of the aluminum in HCl solution in the presence and absence of inhibitors were studied by a DC polarization technique. The test was carried out in an electrochemical cell including aluminum specimen (working electrode), platinum plate (counter electrode) and saturated calomel (reference) electrode. The polarization plots were obtained at sweep rate of 1 mV/s in the range of ±200 mV from the open circuit potential (OCP). The OCP was measured after 1 h (after reaching to steady state). The test was carried out on 1 cm^2 of the samples in 0.25 M HCl solution in the presence and absence of BT and BTH. The electrochemical parameters including corrosion current density (I_{corr}), corrosion inhibition efficiency (\eta) and corrosion rate were obtained from the polarization curves. The corrosion current density (I_{corr}) was obtained using Tafel extrapolation technique and general purpose electrochemical software (GPES).

2.2.3. EIS and EN measurements
Electrochemical impedance spectroscopy (EIS) and electrochemical noise analysis (EN) were utilized to investigate the corrosion inhibition properties of the inhibitors in 0.25 M HCl solution on the aluminum surface. The measurements in EIS test were carried out by an AUTOLAB G1 at perturbation and frequency range of 10 mV and 10 kHz to 10 mHz, respectively. To this end, an electrochemical system including platinum plate (auxiliary electrode), saturated Calomel electrode (reference) and aluminum sheet (working electrode) was used. For the EN analysis, the electrochemical potential and current noise were measured simultaneously by connecting two aluminum panels and Calomel reference electrode to the EN port of the Autolab PGSTAT12. The measurements were made during a period of 1000 s at 1-s intervals (frequency range from 1 mHz to 0.5 Hz). Data were determined by the expressions f_{max} = 1/2 \Delta t and f_{min} = 1/N \Delta t where \Delta t and N are the sample interval and the total number of data recorded, respectively. The DC trend was removed from the measured data before statistical data analysis through moving average removal (MAR) method [27].
Both EIS and EN measurements were carried out on 1 cm$^2$ of the aluminum in 0.25 M HCl solution in the presence and absence of BT and BTH inhibitors. In both EIS and EN techniques, the test was carried out using three replicates to ensure the measurement repeatability.

3. Results and discussion

3.1 DC polarization measurements

The corrosion inhibition properties of the aluminum in 0.25 M HCl solution in the presence and absence of BT and BTH were studied by DC polarization measurements. Variation of potential versus current density of different samples is shown in Figure 2.

Electrochemical parameters including corrosion current density ($I_{corr}$), corrosion potential ($E_{corr}$) and Tafel slopes ($\beta_a$ and $\beta_c$) were obtained from the polarization curves (Figure 2). The results are shown in Table 2.

![Figure 2. Current versus potential of the Al samples exposed to 0.25 M HCl in the presence of (a) BTH and (b) BT inhibitors at different concentrations.](image-url)
Table 2: Electrochemical parameters obtained from polarization measurements for the Al samples exposed to BT and BTH at different concentrations in 0.25 M HCl solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\beta_a$ (mV/decade)</th>
<th>$\beta_c$ (mV/decade)</th>
<th>$E_{corr}$ (mV)</th>
<th>$I_{corr}$ (µA cm$^{-2}$)</th>
<th>corrosion rate (mpy)</th>
<th>$R_p$ (Ω cm$^2$)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 ppm</td>
<td>125</td>
<td>22.9</td>
<td>-665</td>
<td>325</td>
<td>3.0</td>
<td>25</td>
<td>--</td>
</tr>
<tr>
<td>BT-25 ppm</td>
<td>97</td>
<td>17.2</td>
<td>-664</td>
<td>211</td>
<td>2.5</td>
<td>30</td>
<td>35</td>
</tr>
<tr>
<td>BT-50 ppm</td>
<td>95</td>
<td>13.4</td>
<td>-663</td>
<td>166</td>
<td>1.9</td>
<td>35</td>
<td>49</td>
</tr>
<tr>
<td>BT-100 ppm</td>
<td>97</td>
<td>13.4</td>
<td>-669</td>
<td>149</td>
<td>1.7</td>
<td>34</td>
<td>54</td>
</tr>
<tr>
<td>BT-200 ppm</td>
<td>92</td>
<td>14.4</td>
<td>-664</td>
<td>95</td>
<td>1.1</td>
<td>56</td>
<td>70</td>
</tr>
<tr>
<td>BTH-400 ppm</td>
<td>112</td>
<td>17.7</td>
<td>-663</td>
<td>219</td>
<td>2.5</td>
<td>30</td>
<td>32</td>
</tr>
<tr>
<td>BTH-600 ppm</td>
<td>112</td>
<td>19.1</td>
<td>-667</td>
<td>174</td>
<td>2.0</td>
<td>40</td>
<td>46</td>
</tr>
<tr>
<td>BTH-800 ppm</td>
<td>119</td>
<td>19.3</td>
<td>-668</td>
<td>153</td>
<td>1.7</td>
<td>47</td>
<td>52</td>
</tr>
<tr>
<td>BTH-1000 ppm</td>
<td>112</td>
<td>14.2</td>
<td>-668</td>
<td>125</td>
<td>1.4</td>
<td>50</td>
<td>61</td>
</tr>
</tbody>
</table>

Polarization resistance ($R_p$) values were calculated from equation (1):

$$R_p = \frac{(\beta_a \times \beta_c)}{(2.3 \times I_{corr} (\beta_a + \beta_c))} \quad (1)$$

where $R_p$, $\beta_a$, $\beta_c$ and $I_{corr}$ show polarization resistance, anodic Tafel slope, cathodic Tafel slope and corrosion current density, respectively.

As can be seen in Table 2 and Figure 2, the $I_{corr}$ and corrosion rate were reduced in the presence of both inhibitors. The $R_p$ of the aluminum increased significantly when different concentrations of BT and BTH were added to HCl solution. The decrease in $I_{corr}$ and the increase in $R_p$ were more and more pronounced with increasing the inhibitor concentration. These observations reveal that the corrosion inhibitors could efficiently reduce the dissolution rate of aluminum in HCl solution. It can be clearly seen from the results shown in Table 2 that both anodic and cathodic Tafel slopes were reduced with increasing the inhibitors concentration. However, the decrease in anodic current density was not significant. The variations of $\beta_{an}$ and $\beta_{cath}$ in Table 2 indicate the influence of inhibitors on the kinetics of hydrogen evolution and the inhibitor adsorption on the aluminum surface. Results show that the decrease in cathodic current density was higher than anodic one in the presence of both BTH and BT. This observation reveals that these inhibitors could reduce the dissolution rate of aluminum by reducing the cathodic reactions. These observations reveal that the adsorbed inhibitors molecules formed a protective film on the surface of the aluminum. The protective layer could reduce the aluminum dissolution rate significantly. Results showed the lower $I_{corr}$ and higher $R_p$ values of the aluminum sample exposed to the HCl solution containing BT compared with BTH. This can show the higher corrosion protection properties of the aluminum in the presence of BT.

3.2. Electrochemical impedance spectroscopy (EIS) measurements

The corrosion performance of the aluminum in HCl solution in the presence and absence of different concentrations of BT and BTH was also studied by an EIS technique. The Nyquist and Bode plots are shown in Figure 3.

Figure 3 shows that BTH and BT increase the corrosion resistance of the aluminum. The Nyquist plots consist of a capacitive loop at high frequencies and inductive loop at low frequencies. This can demonstrate the common behavior of the aluminum in HCl solution [31-35]. Using electrical circuit shown in Figure 4, the electrochemical parameters including charge transfer resistance ($R_{ct}$), polarization resistance ($R_p$), constant phase element (CPE), inductance resistance ($R_L$), inductor (L) and impedance at 1 Hz were obtained (Table 3). The representative example of using this equivalent circuit to fit the experimental data is shown in Figure 5. The chi-squared ($\chi^2$) is used to evaluate the precision of the fitted data [31].
Figure 3. Nyquist and Bode plots of the samples exposed to 0.25 M HCl solution containing BTH ($a_1$ and $a_2$), and BT ($b_1$ and $b_2$) at different concentrations.

Figure 4. Electrical equivalent circuit used to analyze the results obtained from EIS (Figure 3).
Figure 5. The representative figure of using the equivalent circuit to fit the experimental data for 0.25 M HCl without inhibitor, (a) Nyquist and (b) Bode plots.

Table 3: Electrochemical parameters obtained from EIS measurements for the Al samples exposed to BT and BTH at different concentrations in 0.25 M HCl solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_{ct}$ (Ω cm$^2$)</th>
<th>$Y_0$ (Ω$^{-1}$ cm$^{-2}$)</th>
<th>$h$</th>
<th>$L$ (H cm$^2$)</th>
<th>$R_L$ (Ω cm$^2$)</th>
<th>$C_{dl}$ (μF cm$^{-2}$)</th>
<th>$R_p$ (Ω cm$^2$)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 ppm</td>
<td>86</td>
<td>$3.48 \times 10^{-5}$</td>
<td>0.95</td>
<td>143</td>
<td>38.08</td>
<td>26.44645</td>
<td>26.4</td>
<td>0.008</td>
</tr>
<tr>
<td>BT-25 ppm</td>
<td>106</td>
<td>$3.23 \times 10^{-5}$</td>
<td>0.95</td>
<td>195</td>
<td>44</td>
<td>24.5</td>
<td>31.4</td>
<td>0.001</td>
</tr>
<tr>
<td>BT-50 ppm</td>
<td>152</td>
<td>$3.35 \times 10^{-5}$</td>
<td>0.94</td>
<td>399</td>
<td>73</td>
<td>24.3</td>
<td>49.5</td>
<td>0.007</td>
</tr>
<tr>
<td>BT-100 ppm</td>
<td>207</td>
<td>$3.27 \times 10^{-5}$</td>
<td>0.93</td>
<td>803</td>
<td>142</td>
<td>23.5</td>
<td>84.4</td>
<td>0.005</td>
</tr>
<tr>
<td>BT-200 ppm</td>
<td>264</td>
<td>$2.79 \times 10^{-5}$</td>
<td>0.93</td>
<td>799</td>
<td>140</td>
<td>20.4</td>
<td>91.6</td>
<td>0.006</td>
</tr>
<tr>
<td>BTH-400 ppm</td>
<td>114</td>
<td>$3.44 \times 10^{-5}$</td>
<td>0.94</td>
<td>301</td>
<td>62</td>
<td>24.3</td>
<td>40.4</td>
<td>0.008</td>
</tr>
<tr>
<td>BTH-600 ppm</td>
<td>155</td>
<td>$2.52 \times 10^{-5}$</td>
<td>0.95</td>
<td>322</td>
<td>65</td>
<td>19.4</td>
<td>46.0</td>
<td>0.001</td>
</tr>
<tr>
<td>BTH-800 ppm</td>
<td>212</td>
<td>$2.54 \times 10^{-5}$</td>
<td>0.94</td>
<td>373</td>
<td>73</td>
<td>19.1</td>
<td>54.6</td>
<td>0.008</td>
</tr>
<tr>
<td>BTH-1000 ppm</td>
<td>248</td>
<td>$2.41 \times 10^{-5}$</td>
<td>0.94</td>
<td>349</td>
<td>75</td>
<td>17.4</td>
<td>58.2</td>
<td>0.009</td>
</tr>
</tbody>
</table>
The low $\chi^2$ shown in Table 3 indicates that the fitted data have good agreement with the experimental data.

Double layer capacitance ($C_{dl}$) and polarization resistance ($R_p$) values were calculated according to equations 2 and 3:

\[ C_{dl} = Y_0 (2\pi f_{\text{max}})^{(n-1)} \]  \hspace{1cm} (2)

\[ R_p = (R_i - R_L)/(R_i + R_L) \times 100 \]  \hspace{1cm} (3)

where $C_{dl}$, $f_{\text{max}}$, $Y_0$ and $n$ represent double layer capacitance, frequency at which the imaginary component of the impedance is maximum, admittance constant and the empirical exponent, respectively. The passive film presented on the surface of the aluminum is not stable in HCl solution. As a result, the corrosion resistance of the aluminum in HCl solution is very low in the absence of the inhibitors. Results presented in Table 2 can clearly show the decrease in $C_{dl}$ values and the increase in impedance and $R_p$ in the presence of both inhibitors. It can be seen that the decrease in $C_{dl}$ and the increase in $R_p$ were more pronounced at higher concentrations of both inhibitors. The decrease in $C_{dl}$ in the presence of inhibitors can be attributed to the local dielectric constant reduction and/or the increase in double layer thickness. These observations demonstrate that the adsorption of inhibitors molecules on the surface of the aluminum significantly enhanced its corrosion resistance. The water molecules replacement with adsorbed inhibitor molecules on the metal surface resulted in protective film formation. The large BTH and BT molecules adsorption on the surface of aluminum led to the increase in double layer thickness and therefore the capacitance reduction. Results obtained from EIS analysis show the superior corrosion inhibition properties of BT compared with BTH. This observation reveals that BT molecules could form better protective film on the surface of the aluminum than BTH. The results obtained from EIS analysis are completely in agreement with the results obtained from polarization measurements.

3.3. Electrochemical noise (EN) measurements

Electrochemical noise was utilized in order to investigate the time records of the electrochemical current noise and the corresponding PSD ($I$) plots of the aluminum samples in 0.25 M HCl solutions in the presence and absence of the BT and BTH inhibitors. The results obtained are presented in Figures 6 and 7.

Figure 6 shows lower amplitude of current fluctuations generated in the presence of both inhibitors compared with the HCl solution without inhibitors. This observation reveals that the noise level reduced significantly in the presence of the inhibitors. This finding demonstrates that the inhibitors could reduce the corrosion of aluminum considerably. To calculate the noise resistance, the standard deviation from potential and current were calculated from equations 4 and 5, respectively.

\[ \sigma_E = \sqrt{\frac{\sum_{i=1}^{n} (E_i - m_E)^2}{n}} \quad m_E = \frac{\sum_{i=1}^{n} E_i}{n} \]  \hspace{1cm} (4)

\[ \sigma_i = \sqrt{\frac{\sum_{i=1}^{n} (I_i - m_i)^2}{n}} \quad m_i = \frac{\sum_{i=1}^{n} I_i}{n} \]  \hspace{1cm} (5)

where $\sigma_E$, $\sigma_i$ and $n$ represent the standard deviation of potential noise, the standard deviation of current noise and total number of measurements, respectively. The noise resistance can be calculated from equation 6 [36]. Variation of $R_n$ versus inhibitor concentration is shown in Figure 8.

\[ R_n = \frac{\sigma_E}{\sigma_i} \]  \hspace{1cm} (6)
Investigate Crossion Inhibition Properties

Figure 6. Current noise transients associated with Al samples exposed to 0.25 M HCl solution a) containing 0 and 1000 ppm BTH b) containing 0 and 200 ppm BT.

Figure 7. PSD (f) plots associated with Al samples exposed to 0.25 M HCl solution containing a) 0 to 1000 ppm BTH and b) 0 to 200 ppm BT.
As can be seen in Figure 8, the $R_n$ was increased in the presence of both inhibitors. The increase in $R_n$ was more pronounced at higher inhibitors concentrations. It can be obviously seen that the increase in $R_n$ was more and more pronounced in the case of using BT. This observation reveals the higher corrosion inhibition efficiency of BT compared with BTH. Also, these results are completely in agreement with the results obtained from the EIS and polarization measurements.

The shot noise theory [37] was employed to analyze EN data by considering current noise signals as packets of charge ($q$). The characteristic charge can be calculated from equation 7.

$$q = \sqrt{\Psi_E} \sqrt{\Psi_I} / B$$

(7)

where $\Psi_E$, $\Psi_I$, and $B$ are low frequency PSD value of potential, low frequency PSD value of current and the Stern-Grey coefficient (the average value about 0.026 V), respectively.

It should be noted that in the case of aluminium alloy, the corrosion is likely to be localized and this may limit the applicability of the Stern-Geary coefficient. However, the localized corrosion is not that much significant for the aluminium alloy used in this study. Therefore, the Stern-Grey coefficient is applicable.

The characteristic charge ($q$) can provide useful information on mass loss during corrosion process in the presence and absence of BTH and BT [34, 35]. Variation of characteristic charge ($q$) versus inhibitor concentration is studied in Figure 9.

As can be seen in Figure 9, the characteristic charge ($q$) was reduced in the presence of both inhibitors. It can be obviously seen that the decrease in $q$ was more and more pronounced at higher inhibitors concentrations. Results show that BT reduced characteristic charge ($q$) much greater than BTH. This observation reveals that the inhibitors could reduce oxidation rate of aluminum in HCl solution. This can be responsible for the $q$ reduction on the surface of aluminum. The adsorption of inhibitors molecules on the surface of aluminum can be responsible for the characteristic charge reduction.

3.4. Scanning electron microscope (SEM) studies

SEM was utilized in order to investigate the aluminum surface morphology changes in the HCl solution in the presence and absence of the inhibitors. The SEM micrographs are shown in Figure 10.

Figure 10b shows a rough surface with corrosion products of aluminum after exposure to the HCl solution in the absence of inhibitors. This observation
reveals that HCl solution destroyed the aluminum surface significantly in the absence of inhibitors. However, addition of inhibitors to the HCl solution changed the visual performance of the surface of aluminum considerably. Figures 10c and 10d show that dissolution rate of aluminum was considerably reduced in the presence of both BT and BTH inhibitors. It can be seen that inhibitors have formed a protective film on the metal surface. However, the surface of sample exposed to HCl solution containing BT is smoother than the one containing BTH. Moreover, BT formed better passive film on the surface of aluminum. These results could support higher inhibition efficiency of BT compared with BTH.

Figure 9. Variation of characteristic charge ($q$) versus inhibitor concentration.

Figure 10. SEM micrographs of (a) blank Al sample before exposure to 0.25 M HCl (b) Al sample exposed to 0.25 M HCl, (c) Al sample exposed to 0.25 M HCl containing 1000 ppm BTH and (d) 200 ppm BT.


3.5. Corrosion inhibition efficiency evaluation

Results obtained from DC polarization, EIS and EN showed that the corrosion resistance of aluminum was enhanced in the presence of inhibitors in HCl solution. There was a good agreement between the results of various techniques. The corrosion inhibition efficiency values were calculated according to equations 8 to 10

\[
\text{EF\%} = (1 - \frac{I}{I_0}) \times 100
\]

where EF\%, \(I_0\) and \(I\) represent corrosion inhibition efficiency, corrosion current density in the absence of the inhibitors, and corrosion current density in the presence of corrosion inhibitors, respectively.

\[
\text{EF\%} = \left(\frac{R_{ct} - R_{ct}^0}{R_{ct}}\right) \times 100
\]

where \(R_{ct}\) and \(R_{ct}^0\) show charge transfer resistance in the presence and absence of the inhibitors, respectively.

\[
\text{EF (ECN)\%} = \left(\frac{R_n - R_n^0}{R_n^0}\right) \times 100
\]

where \(R_n\) and \(R_n^0\) represent noise resistance of the inhibited and uninhibited specimens, respectively. Variations of \(\text{EF (\%)}\), calculated in DC, EIS and EN measurements, versus inhibitor concentration are shown in Figure 11.

As can be seen in Figure 11, the increase of inhibitors concentrations resulted in the increase in corrosion resistance of aluminum in 0.25 M HCl solution. The corrosion inhibition values \(> 0.6\%\) and \(> 0.7\%\) were obtained for the BTH and BT inhibitors, respectively. The same results were obtained in DC, EIS and EN measurements. It can be clearly seen that the corrosion inhibition values obtained in EN measurement (for BT) are higher than those obtained in DC and EIS measurements. However, the same trend can be seen for all the measurements. Two main reasons may be responsible for the higher corrosion inhibition efficiency obtained from EN compared with EIS and DC polarization. First, the experimental duration for the polarization measurement (which was about 10 min) was lower than the impedance study and EN (which were about 13 and 17 min, respectively). The higher experimental duration of the EN compared to DC polarization and EIS may increase the adsorption of inhibitor molecules on the metal surface [36].

As a result, the corrosion inhibition efficiency obtained from EIS and polarization measurements were lower than EN. The second reason is that noise resistance values obtained from EN are higher than polarization resistance values obtained from DC polarization and EIS. This may be attributed to the differences between the techniques for the evaluation of corrosion resistance of the metal in HCl solution. Other researchers also showed the same findings that noise resistance is greater than polarization resistances obtained from EIS and DC measurements [39].

It seems that the results obtained from the noise measurements are more accurate and reliable compared with EIS and DC polarization. Unlike EIS and DC polarization techniques, no external perturbation was applied to the samples during the measurements. Electrochemical noise data can be obtained from the appearance of fluctuations, statistical analysis and also shot noise theory. This means that EN data is more accurate than other electrochemical techniques.

3.6. Adsorption isotherm and inhibition mechanism of the inhibitors

The BTH and BT molecules have high tendency to be adsorbed on the surface of aluminum. The adsorption of inhibitor molecules on the metal surface occurs through water molecules replacement with organic inhibitors molecules. The mechanism is shown by equations 11 and 12 [40].

\[
\text{BTH}_{\text{sol}} + \text{H}_2\text{O}_{\text{ads}} \rightarrow \text{BTH}_{\text{ads}} + \text{H}_2\text{O}_{\text{sol}}
\]

(11)

\[
\text{BT}_{\text{sol}} + \text{H}_2\text{O}_{\text{ads}} \rightarrow \text{BT}_{\text{ads}} + \text{H}_2\text{O}_{\text{sol}}
\]

(12)
Valuable information on the interaction of inhibitor and metal surface can be obtained by studying the mode of adsorption and adsorption isotherm. The experimental results were fitted to a series of adsorption isotherms including Langmuir [41], Frumkin [42], Temkin [43, 44] and Freundlich [45] (Figure 12). These isotherms are defined by equations 13 to 16.

\[ C\text{(ads)}\theta = \frac{1}{K\text{(ads)}} + C\text{(ads)} \]  
(Langmuir isotherm)  
(14)

\[ \ln \frac{A}{(C\text{(ads)})(1 - \theta)} = \ln K + 2a\theta \]  
(Frumkin isotherm)  
(15)

\[ \ln \theta = \log K + \frac{1}{n \log C\text{(ads)}} \]  
(Freundlich isotherm)  
(16)
where \( \theta, C(\text{ads}) \) and \( K(\text{ads}) \) are the degree of coverage on the metal surface, inhibitor concentration and the equilibrium constant for the adsorption-desorption process, respectively.

The correlation between \( K(\text{ads}) \) and \( \Delta G^\circ(\text{ads}) \) is shown in equation 17:

\[
\Delta G^\circ = RT \ln(55.5 \cdot K(\text{ads}))
\]

(17)

where \( R \) and \( T \) are the universal gas constant and the absolute temperature respectively. \( K(\text{ads}) \) and \( \Delta G^\circ(\text{ads}) \) were obtained from EN, EIS and potentiodynamic measurements. Moreover, the regression coefficients were calculated from each isotherm and the results obtained are shown in Tables 4 and 5.

As can be seen in Tables 4 and 5, the regression coefficient values obtained from Langmuir adsorption isotherm are greater than the results obtained from other isotherms (Figure 12). This observation shows that the adsorption of BT and BTH molecules on the surface of aluminum obeys a Langmuir adsorption isotherm.

![Figure 12](image_url)

**Figure 12.** Different adsorption isotherms fitted on EIS results of Al samples exposed to 0.25 M HCl solution containing different concentrations of BTH and BT.
Table 4: The values of standard free energy of adsorption (ΔG°(ads)) and regression coefficient (R²) for the adsorption–desorption process obtained from different isotherms for BT and BTH inhibitors.

<table>
<thead>
<tr>
<th>Sample</th>
<th>∆G°(ads) (kJ)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EIS</td>
<td>DC</td>
</tr>
<tr>
<td>BT (Langmuir)</td>
<td>-28.0</td>
<td>-29.0</td>
</tr>
<tr>
<td>BTH (Langmuir)</td>
<td>-22.7</td>
<td>-22.5</td>
</tr>
<tr>
<td>BT (Frumkin)</td>
<td>-28.6</td>
<td>-32.5</td>
</tr>
<tr>
<td>BTH (Frumkin)</td>
<td>-23.8</td>
<td>-22.8</td>
</tr>
<tr>
<td>BT (Temkin)</td>
<td>-33.3</td>
<td>-36.0</td>
</tr>
<tr>
<td>BTH (Temkin)</td>
<td>-27.8</td>
<td>-26.7</td>
</tr>
<tr>
<td>BT (Freundlich)</td>
<td>-18.1</td>
<td>-13.9</td>
</tr>
<tr>
<td>BTH (Freundlich)</td>
<td>-14.6</td>
<td>-16.7</td>
</tr>
</tbody>
</table>

Table 5: The values of equilibrium constant (K(ads)) and regression coefficient (R²) for adsorption–desorption process obtained from different adsorption isotherms for BT and BTH inhibitors.

<table>
<thead>
<tr>
<th>Sample</th>
<th>K(ads) (M⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EIS</td>
<td>DC</td>
</tr>
<tr>
<td>BT (Langmuir)</td>
<td>1.6×10⁴</td>
<td>2.5×10³</td>
</tr>
<tr>
<td>BTH (Langmuir)</td>
<td>1.8×10⁴</td>
<td>1.7×10³</td>
</tr>
<tr>
<td>BT (Frumkin)</td>
<td>2.1×10⁴</td>
<td>1.0×10³</td>
</tr>
<tr>
<td>BTH (Frumkin)</td>
<td>2.9×10⁴</td>
<td>2.0×10³</td>
</tr>
<tr>
<td>BT (Temkin)</td>
<td>1.4×10⁴</td>
<td>4.3×10³</td>
</tr>
<tr>
<td>BTH (Temkin)</td>
<td>1.5×10⁴</td>
<td>9.9×10³</td>
</tr>
<tr>
<td>BT (Freundlich)</td>
<td>29.9</td>
<td>5.3</td>
</tr>
<tr>
<td>BTH (Freundlich)</td>
<td>6.9</td>
<td>16.9</td>
</tr>
</tbody>
</table>

Table 4 shows the higher free energy of adsorption for the BT compared with BTH. This observation reveals the higher adsorption of BT molecules on the surface of metal compared with BTH. The negative values of ∆G°(ads) show the spontaneous adsorption of BTH and BT molecules on the surface of aluminum. Table 5 shows higher K(ads) for the BT compared with BTH. These results indicate that BT is a better inhibitor for the aluminum protection against corrosion in HCl solution compared with BTH. The BTH and BT inhibitors include heteroatoms (N and S). Therefore, the coordination between BTH and BT molecules and the surface of aluminum can occur via N and S atoms. The BTH and BT molecules can be oriented parallel or vertical to the metal surface. Stronger bonds between inhibitors molecules and aluminum surface can be formed when the orientation of the inhibitor molecule is parallel to the aluminum surface. This can be attributed to the interaction of p electrons of the ring with vacant d orbitals of aluminum. In this way, the inhibitors molecules tend to be adsorbed by the aluminum surface and form complex film on the metal surface.

It has been shown that ∆G°(ads)= -20 kJ mol⁻¹ or ∆G°(ads)< -20 kJ mol⁻¹ are associated with an electrostatic interaction between charged molecules and charged metal surface (physical adsorption) [43-44]. On the other hand, ∆G°(ads)= -40 kJ mol⁻¹ or ∆G°(ads)> -40 kJ mol⁻¹ are associated with charge
sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate covalent bond (chemical adsorption) [46, 47]. The values of standard free energy of adsorption between -40 kJ mol\(^{-1}\) \(<\Delta G^\circ\text{(ads)}\)<-20 kJ mol\(^{-1}\) show mixed type adsorption (both chemical and physical interactions). Based on these explanations and the results shown in Tables 4 and 5, it can be found that the adsorption of BTH and BT molecules on the surface of aluminum occurred through both chemical and physical interactions. However, \(\Delta G^\circ\text{(ads)}\) values of BTH are more close to -20 kJ mol\(^{-1}\). Therefore, the adsorption of BTH on the surface of aluminum is predominantly physisorption. On the other hand, \(\Delta G^\circ\text{(ads)}\) values of BT are close to -30 kJ mol\(^{-1}\) indicating more chemical interactions between this inhibitor and metal surface compared with BTH. BT includes 3 N atoms but BTH consists of one N and one S atom. The higher number of nitrogen atoms of BT than BTH can be responsible for the greater ability of this inhibitor to produce stronger physical/chemical bonds with the metal surface.

4. Conclusions
The corrosion inhibition properties of BTH and BT on aluminum in 0.25 M HCl solution were studied. The corrosion protection properties of the inhibitors were studied by analytical techniques including EIS, EN and DC polarization. Results showed good corrosion inhibition effects of BTH and BT on aluminum in 0.25 M HCl solution. The corrosion current density of aluminum in 0.25 M HCl was significantly increased in the presence of both inhibitors. Results showed higher corrosion inhibition properties of BT compared with BTH. The EN measurements revealed that both inhibitors increased noise resistance (\(R_n\)) and reduced characteristic charge (\(q\)) significantly. The increase in \(R_n\) and the decrease in characteristic charge (\(q\)) were more pronounced in the presence of BT compared with BTH. It was found that the best fit to the experimental data was Langmuir adsorption isotherm. The adsorption of both inhibitors on the surface of aluminum was based on physical and chemical adsorption (covalent bond). The high values of \(K\text{(ads)}\) and negative values of \(\Delta G\text{(ads)}\) suggested that BT and BTH molecules highly tended to be adsorbed on the surface of aluminum. The greater \(K\text{(ads)}\) and more negative \(\Delta G\text{(ads)}\) values of BT compared with BTH were observed.

5. References
Investigate Crossion Inhibition Properties


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