Effectiveness of 2-mercaptobenzothiazole, 8-hydroxyquinoline and benzotriazole as corrosion inhibitors on AA 2024-T3 assessed by electrochemical methods

Andronikos C. Balaskas,* Michele Curioni and George E. Thompson

In this study, the effectiveness of 2-mercaptobenzothiazole (2-MBT), 8-hydroxyquinoline and benzotriazole as corrosion inhibitors for AA 2024-T3 aluminium alloy was evaluated. The corrosion behaviour in the presence of each compound was investigated by image-assisted electrochemical noise analysis, electrochemical impedance spectroscopy, potentiodynamic polarization and the split cell technique. It was found that 2-MBT has superior inhibition properties compared with the other inhibitors. In particular, the specimens immersed in 3.5% NaCl in the presence of 2-MBT displayed high values of noise resistance that were maintained for over 400 h of testing, and high values of low-frequency impedance, measured after immersion for 24 h. The split cell technique and potentiodynamic polarization tests indicated that only 2-MBT decreases significantly both the anodic and the cathodic reaction rates. Scanning electron microscopy observations and energy dispersive X-ray measurements complement the findings from electrochemical measurements indicating that only 2-MBT protects the second phase particles, preventing dealloying, trenching and initiation of corrosion. © 2015 The Authors. Surface and Interface Analysis published by John Wiley & Sons Ltd.

Keywords: AA 2024-T3; inhibitors; electrochemical noise; EIS; potentiodynamic polarization

Introduction

Hexavalent chromium is a widely used inhibitor for corrosion protection of aluminium alloys. However, development of more environment-friendly inhibitors is a necessity because hexavalent chromium is responsible for cancer and many environmental concerns.[1,2] For this reason, environment-friendly, organic inhibitors are studied as potential hexavalent chromium replacements.

Various organic compounds with thiazole and triazole groups have been studied previously as corrosion inhibitors for aluminium alloys.[3–9] 2-Mercaptobenzothiazole has been found to be effective for long-term corrosion protection of AA 2024-T3, because it decreased the rate of both the anodic and cathodic reactions as suggested by polarization tests in low concentration (0.05 and 0.005 M) NaCl solutions.[3,10] 2-Mercaptobenzothiazole was also used to load nanocontainers incorporated in sol–gel films for protection of AA 2024 substrates.[11] The inhibiting properties of 2-mercaptobenzothiazole on copper have been studied by Raman spectroscopy and linear voltammetry.[12] The results showed that the presence of 2-MBT inhibits the anodic dissolution of copper by formation of a complex between the oxidized form of 2-MBT and copper ions leading to a polymeric layer on the substrate. The formation of a film between copper oxides and the ionized form of copper ions leading to a polymeric layer on the substrate. The formation of a complex between the oxidized form of 2-MBT and copper ions leading to a polymeric layer on the substrate.

The effect of 8-hydroxyquinoline on corrosion of pure aluminium was studied by polarization curves, electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy in 0.5 M NaCl solution.[15] The findings suggest the formation of a complex of aluminium and 8-hydroxyquinoline on the surface, behaving as a passive layer. Further, the inhibiting action of 8-hydroxyquinoline on copper substrates, because of the formation of a protective film composed of Cu(II)-8-hydroxyquinoline complexes, has been described previously.[16] 8-Hydroxyquinoline has also been studied as a corrosion inhibitor for AA 2024-T3 substrates in 0.05 M NaCl solution.[13] The results from EIS and X-ray photoelectron spectroscopy indicated the formation of a film of insoluble complexes, which acted as a protective layer. The absorption of insoluble complexes was also reported to occur on the S-phase particles, protecting the alloy by preventing the selective dissolution of Mg and Al within the S-phases, thus preventing cathodic activation.

Benzotriazole has functional polar groups (nitrogen) and conjugated double bonds. Benzotriazole has been reported to act as a corrosion inhibitor for copper in different corrosive environments.
environments.17–21 The interaction of benzotriazole with copper oxides, through the functional groups, results in the formation of a complex that is adherent to the substrate and acts as a barrier for corrosive species.22 Benzotriazole has been incorporated into sol–gel coatings on aluminium alloy substrates to prevent corrosion.22 Sol–gel coatings with nanocontainers loaded with benzotriazole have also been used for corrosion protection of aluminium alloys.23

By using image-assisted electrochemical noise (EN) analysis, the time evolution of noise resistance and noise impedance, and the images of the corroding surface can be obtained.24–28 EN measurements were employed previously in order to evaluate the corrosion protection of AA 2024-T3 by benzotriazole.27 It was found that the inhibitor was efficient in low concentrations of chloride solution (0.1 and 0.001 M NaCl) because the value of noise resistance was higher compared with the solution without inhibitor. Selected inhibitors, including sodium nitrate, sodium molybdate and 2-mercaptopurinimidine, were tested for corrosion protection of AA 6351 electrodes using electrochemical noise.20

Also, the anticorrosive properties of sodium chromate, cerium nitrate and benzotriazole were previously studied by image-assisted electrochemical noise.24

Using the split cell technique, the effect of the inhibitor on the anodic and the cathodic reactions as a function of time can be estimated.24 With this technique, the net current and the potential are measured between two identical electrodes immersed in separated cells, connected with a porous glass frit.29,30 By introduction of nitrogen gas in one compartment, the corresponding electrode becomes a net anode; at the same time, air flow in the other compartment results in the corresponding electrode becoming a net cathode. The injection of the tested inhibitor into one of the compartments provides information about its effect on the anodic or the cathodic reaction rates, because inhibition is revealed by a reduction of the values of the measured current.24 For example, the mechanism of corrosion inhibition of AA 2024-T3 by vanadates has been studied by this technique.29 The inhibiting properties of sodium chromate, cerium nitrate and benzotriazole were also studied previously by the split cell technique.24

In the present work, we report a comparative study between the corrosion inhibitors 2-MBT, benzotriazole (BTZ) and 8-HQ in an environment with high concentration of chlorides (3.5% NaCl) and a low concentration of inhibitor (5 mM). Image-assisted EN enables long-term testing and provides the noise resistance as a function of time together with images of the corroding surface. The effect of the inhibitors on the corrosion process is investigated by EIS, and the spectra are analysed with equivalent circuits. With the polarization curves and the split cell technique, the influence of the inhibitors on the anodic and cathodic reactions rates is evaluated. Scanning electron micrographs (SEM) and energy dispersive X-ray (EDX) measurements also display the effects of the inhibitors on the surface and on the second phase particles of the AA 2024-T3 alloy.

**Experimental details**

**Materials and reagents**

AA 2024-T3 electrodes with nominal composition in wt.% of Si <0.5, Fe <0.5, Cu 3.8–4.9, Mn 0.3–0.9, Mg 1.2–1.8, Cr <0.1, Zn <0.25, Ti <0.15 and Al balance, of 1.6 mm thickness were used for all the experiments. The selected inhibitors, 2-mercaptobenzothiazole (2-MBT), BTZ and 8-hydroxyquinoxoline (8-HQ) were of analytical reagent grade and purchased from Sigma-Aldrich (St. Louis, USA).

**Specimen preparation and corrosion evaluation**

The AA 2024-T3 electrodes were pretreated by etching and desmutting. The specimens were initially immersed in 10% w/v NaOH for 30 s at 60°C with stirring. Subsequently, they were rinsed with distilled water and immersed in 30 vol.% HNO₃ for 30 s at room temperature. Finally, the specimens were rinsed with deionized water and dried in a cool air stream. Beeswax was used to mask the specimens such that the exposed surface area during the corrosion tests was 2.25 cm².

For EN measurements, two AA 2024-T3 electrodes were electrically coupled by using a 10 kohm resistor. The potential of each electrode was recorded by an NI-USB6009 (National Instrument) analogue to digital converter, with respect to a saturated calomel electrode (SCE) placed in the corrosive environment. This method for this type of EN measurement is described in detail in Chin et al.29 An in-house developed software, based on Labview programming language, was used to acquire and record the potential noises and to calculate the current noise. The data acquisition was performed at 1023 Hz, in a block of 1000 points at each iteration. Subsequently, the values in one block were averaged to obtain a time record with one value of potential and current per second. The noise resistance values were calculated according to the mathematical procedure described in Curioni et al.24 The images of the corroding surface were acquired by Maplin USB microscopes. The time interval between subsequent image acquisitions was 10 min.

For the EIS measurements a SI 1287 Solartron electrochemical interface, connected with an SI 1250 impedance/frequency response analyser, was used. The measurements were performed at the open circuit potential, using a three-electrode electrochemical cell, comprising the working electrode, a SCE and a platinum foil with area of 1 cm² as the counter electrode. The frequency range inspected was between 10 kHz and 5 mHz, and the rms voltage was 10 mV. The resulting EIS spectra were fitted using the z-view software.

The split cell comprised two cylindrical compartments connected by a porous glass frit in order to enable current flow within the electrolyte, but preventing significant exchange of chemical species between the two compartments. Two nominally identical alloy specimens were immersed in each compartment of the cell and connected through a zero resistance ammeter (ZRA) (Solartron 1280). At the beginning of the experiment, the electrolyte was naturally aerated 1 l of 3.5% NaCl. The alloy specimens were immersed simultaneously and left under naturally aerated conditions for 15 min with mild stirring. Subsequently, nitrogen was passed into one compartment and air into the other. This resulted in the generation of a net anode (nitrogen compartment) and a net cathode (air compartment). After 30 min from commencement of the experiment, the selected inhibitor was added to one of the two compartments.

Potentiodynamic polarization tests were performed at room temperature, using a three-electrode cell consisting of the AA 2024-T3 working electrode (exposed area of ≈2.25 cm²), a saturated calomel electrode (SCE) as the reference electrode, and a platinum electrode (with an area of 1 cm²) as the counter electrode. The test environment was 1 l of naturally aerated 3.5 wt.% NaCl. The pH of the sodium chloride solution was 5.58, whereas the additions of 2-MBT and 8-HQ resulted in pH 4.91 and 6.62, respectively. The solution containing BTZ had a pH of 5.23 at room temperature. 2-MBT is only sparingly soluble in water at neutral pH and, the powder appears to be hydrophobic and therefore, when added to the solution, it tends to stay on the surface. However, 2-MBT is highly soluble in ethanol. By dissolving the 2-MBT in 10 ml of EtOH and
then adding the mixture to the NaCl solution, it is ensured that the latter is saturated and that the excess precipitates at the bottom of the container. With this method, a nominal concentration of 2-MBT of 5 mM is added to the NaCl solution. 8-HQ was not dissolved in EtOH, because it did not display the hydrophobic behaviour, and the sodium chloride solution could be readily saturated with a nominal concentration of 5 mM. This was evident because the colour of the solution became pale yellow after the addition. For anodic polarization, the potential was varied between −0.05 V versus the open circuit potential (OCP) to −0.3 V versus SCE and for cathodic polarization, from the OCP to −1 V versus SCE. The scan rate was 0.10 mV/s. The measurements were undertaken after 24 h of immersion in 3.5% NaCl solution in the presence of the inhibitors.

The reproducibility of the results and the reliability of the experimental setups were evaluated by repeating all the electrochemical measurements two or three times. The average of the noise resistance values for the entire duration of the measurement presented maximum variations of ±10% for measurements performed under nominally identical conditions. Concerning the anodic and cathodic potentiodynamic polarization curves, a maximum difference of ±30% in the current response was observed. EIS measurements presented an error of the fitted values with a maximum difference of ±45%.

Scanning electron microscopy

AA 2024-T3 specimens were prepared by mechanical polishing with 1 μ diamond paste in order to create a flat surface. The specimens were immersed in the 3.5% NaCl solution with the inhibitor for 6 h, then rinsed with distilled water and dried in a cool air stream. The surfaces of the corroded specimens were examined in a Zeiss Ultra 55 field emission gun SEM operated in the acceleration voltage range between 1 and 1.5 kV with a working distance below 3 mm at 0° angle of tilt.

Results

Corrosion tests

Image-assisted electrochemical noise

The protective performance of each inhibitor against corrosion was studied with image-assisted electrochemical noise. The time evolution of the noise resistance of AA 2024-T3 with the addition of the 2-MBT, BTZ and 8-HQ organic inhibitors compared with the specimen immersed in the absence of the inhibitor in 3.5% NaCl solution are presented in Fig. 1(a). Figure 1(b) shows the corresponding optical images acquired during the measurement. After 60 h of immersion, 2-MBT provided exceptional corrosion protection properties because the values of noise resistance were approximately eight times higher than those measured from the specimen immersed in the absence of the inhibitor and the surface appeared uncorroded without any evident darkening or initiation of pitting. The surface of the specimen immersed without inhibitor darkened from the early hours of immersion as a result of the accumulation of copper on the surface. After 60 h of immersion, the dark areas displayed a more intense grey colour as the corrosion progressed.

The addition of BTZ in the corrosive environment resulted in noise resistance values slightly higher than the values obtained for the specimen immersed without inhibitor, and without any signs of pitting or darkening as observed from the optical images until 60 h of testing. In the case of 8-HQ, the noise resistance had similar values to that measured for the specimen without inhibitor. In the case of 8-HQ, the specimen presented pits from 10 h of immersion; until 60 h, the number of pits increased, similarly to the specimen immersed in the absence of the inhibitor.

The time evolution of the noise resistance for a long-term EN measurement, with the corresponding images, for a test in the presence of 2-MBT is presented in Fig. 2. It is evident that the noise resistance maintained a very high value for over 400 h, indicating excellent inhibition properties of 2-MBT. The surface of the specimens did not display pits until 400 h when a small number of pits started to appear present (Fig. 2(b)).

Electrochemical impedance spectroscopy

Figure 3 presents the impedance spectra obtained after 24 h of immersion in 3.5% NaCl with and without inhibitors. The addition of 2-MBT and BTZ to the NaCl solution increased the low frequency impedance value compared with the reference measurement obtained in the absence of the inhibitor, indicating a higher resistance to corrosion. The spectrum corresponding to the addition of 8-HQ is closely similar to the spectrum obtained for the specimen immersed in the absence inhibitor, indicating poor protective properties.

In order to extract quantitative parameters from the EIS spectra, fittings were performed by using the circuit displayed in Fig. 4. The equivalent circuit used to fit the experimental data was selected based on the surface of the AA 2024-T3 undergoing corrosion as shown in the schematic representation in Fig. 4(a). The major part of the alloy matrix is covered by an aluminium oxide layer, which provides a capacitive contribution to the equivalent circuit (Coxide). The presence of corrosion products above active corrosion sites are accounted for by the resistance Rcorr. Such corrosion products are readily revealed by SEM and are present on the specimen immersed in the solution without inhibitor (Fig. 10) nearby the second phase particles of the specimens immersed in the presence of BTZ and 8-HQ (Figs 12 and 13). The active corrosion sites are represented by the parallel between the polarization resistance (Rpol) connected in series with a Warburg (W) accounting for diffusion of oxygen and metallic cations and the double layer capacitance (CPEdl). Examples of active corrosion sites are evident in Figs 10, 12 and 13. Figure 4 (a) provides a schematic representation of the corroding surface and highlight the physical meaning of the equivalent circuit described above. In Fig. 3, the solid lines represent the simulated impedance spectra obtained with the parameters reported in Table 1.

The aluminum oxide capacitance is in the range from 11.6 to 20.8 μF cm², and the corrosion products resistance ranges from 1.9 to 202 Ω cm². The polarization resistance in the case of the specimen without inhibitor and 8-HQ has values close to 1.2 kΩ cm², and with addition of 2-MBT and BTZ, it is increased to 31.8 and 9.2 kΩ cm², respectively. The double-layer capacitance for the specimen without inhibitor and 8-HQ has values of approximately 150 μF cm² that decrease with addition of 2-MBT and BTZ to values of 20.9 and 49.1 μF cm². When a dielectric layer is formed on the surface, the distance of charge separation at the interface increases. Considering that the capacitance of a parallel plate capacitor decreases with increase of the distance between the plates, a decrease in the measured value of capacitance can be related to the formation of a protective layer on the surface.

Split cell

In order to obtain information on the mechanism of corrosion inhibition provided by various compounds, split cell experiments were performed. After the immersion of the specimens in the two

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Figure 1. (a) Time evolution of the noise resistance and (b) optical images acquired during electrochemical noise measurement for AA 2024-T3 without inhibitor, 2-mercaptobenzothiazole (2-MBT; saturated), 5 mM benzotriazole (BTZ) and 8-hydroxyquinoline (8-HQ; saturated) in 3.5% NaCl solution until 60 h of immersion.
compartments, a current density close to 0 was observed. After 15 min, nitrogen gas flow was commenced in one of the compartments, and the corresponding specimen progressively became a net anode because of the removal of oxygen and consequent suppression of the oxygen reduction reaction. The other electrode, located in the compartment with air flow, because of the availability of oxygen, became a net cathode. The current measured at this stage was generally of the order of 0.6 μA cm⁻².

Similar to the EN experiments, a control test was performed in the absence of any corrosion inhibitor (Fig. 5).

The addition of 2-MBT in the anodic compartment induced a rapid current density drop and a corresponding increase of potential. The same addition to the cathodic compartment resulted in a less rapid decrease of the current and in a progressive increase of the potential (Fig. 6). The same experiments were also performed for the other organic inhibitors. The addition of BTZ in the anodic side induced a fast decrease of the current and a corresponding increase of the potential. However, after the addition to the cathodic compartment, no changes of the current and the potential were observed (Fig. 7). With the addition of 8-HQ into the anodic and the cathodic compartment, the current and the potential were unaffected, presenting stable values until the end of the experiment (Fig. 8). The split cell experiments enable to evaluate the time required for the inhibition to take place. In particular, in Fig. 6, it is evident that the addition of 2-MBT to the anodic compartment resulted in a progressive decrease in current, suggesting that some time is required before a protective film is generated on the active anodic sites. The relatively irregular steps in current might be due to the deactivation of some of the active corroding sites on the alloy surface, and also affected by the hydrodynamic regime during the split cell experiment, involving both stirring and nitrogen purging.

**Potentiodynamic polarization curves**

The anodic and cathodic polarization curves for various inhibiting solutions after 24 h of immersion in the corrosive environment are presented in Fig. 9. Addition of 2-MBT to the corrosive solution resulted in a significant reduction of both anodic and cathodic current densities of more than one decade compared with the specimen immersed without inhibitor. The presence of 5 mM BTZ decreased the anodic current of about one decade, but the...
Cathodic reaction rate presented similar values compared with the experiments conducted in the absence of the inhibitor. In the case of 8-HQ, both anodic and cathodic current densities are similar to the values measured without inhibitor. For all the tested inhibitors, the pitting potential did not change compared with the specimen immersed in the absence of the inhibitor. The fluctuations in the current close to the OCP are caused by the corrosion events on the surface of the aluminium alloy and are in the range of μA. Such fluctuations are similar to those recorded during EN measurement at the free corrosion potential.

**Table 1.** Fitting parameters for AA 2024-T3 in the presence of 2-MBT, BTZ, 8-HQ and without inhibitor in 3.5% NaCl solution

|                | No inhibitor | 2-MBT | BTZ | 8-HQ |
|----------------|--------------|-------|-----|------|
| $R_{\text{sol}}$ | 3.46         | 4.59  | 4.67| 3.47 |
| $C_{\text{oxide}}$ | 163         | 20.9  | 40.1| 133  |
| $R_{\text{corr pr}}$ | 1.88         | 176   | 202 | 3.71 |
| $C_{\text{dl}}$ | 20.8         | 11.6  | 15.5| 15.1 |
| $R_{\text{pol}}$ | 0.755        | 0.811 | 0.884| 0.806|
| $W_{\text{c}-R}$ | 1262        | 31755 | 9161| 1579 |
| $W_{\text{c}-T}$ | 9868        | 35324 | 14377| 11772|
| $W_{\text{c}-P}$ | 395         | 69.5  | 41.9| 533  |
| $\chi^2$ | $5.89 \times 10^{-3}$ | $4.2 \times 10^{-3}$ | $6.89 \times 10^{-3}$ | $1.44 \times 10^{-3}$ |

2-MBT, 2-mercaptobenzothiazole; BTZ, benzotriazole; 8-HQ, 8-hydroxyquinoline.

**Figure 4.** (a) Schematic representation of the corroding surface and (b) the equivalent circuit model used for the description of the corroding process on the right.

**Figure 5.** Time evolution of (a) current and (b) potential during a split cell test for AA 2024-T3 without addition of inhibitors in 3.5% NaCl solution.
The values of \( i_{\text{corr}} \) and \( E_{\text{corr}} \) obtained from the potentiodynamic polarization curves are presented in Table 2. Addition of 2-MBT resulted in the most significant current density reduction followed by BTZ, while 8-HQ displayed similar values compared with the specimen immersed in the absence of the inhibitor. The Stern–Geary coefficient, \( B \), was calculated according to Eqn (1).[^31] The anodic Tafel coefficient, \( \beta_a \), was calculated above the pitting potential and the cathodic Tafel coefficient, \( \beta_c \), was estimated by considering the Tafel slope of the cathodic current before the onset of diffusion control. The corrosion current (\( i_{\text{corr}} \)) and the corrosion potential (\( E_{\text{corr}} \)) were obtained from the intersection of the lines extrapolated from the linear part of the anodic and cathodic potentiodynamic polarization curves. The corrosion current density from the EN and the EIS measurements was calculated according to Eqn (2).[^31] The values are presented in Table 2.

\[
B = \frac{\beta_a \beta_c}{2.303 (\beta_a + \beta_c)} \tag{1}
\]

\[
i_{\text{corr}} = \frac{B}{R^*} \tag{2}
\]

where \( R^* \) is equal to \( R_p \) and \( R_{\text{total}} \) when the \( i_{\text{corr}} \) is calculated in the case of EN and EIS measurements, respectively.

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**Figure 6.** Time evolution of (a) current and (b) potential during the split cell test for AA 2024-T3 with addition of 2-mercaptobenzothiazole (2-MBT) in the anodic and in the cathodic compartment in 3.5% NaCl solution. Arrows are indicating the time of addition of the inhibitor.

**Figure 7.** Time evolution of (a) current density and (b) potential during the split cell test for AA 2024-T3 with addition of 5 mM benzotriazole (BTZ) in the anodic and in the cathodic compartments in 3.5% NaCl solution. Arrows are indicating the time of addition of the inhibitor.
The surface morphology of AA 2024-T3 after immersion in 3.5% NaCl solution with and without inhibitors was examined by SEM. Figure 10 shows an image of AA 2024-T3 after 6 h immersion in 3.5% NaCl, revealing trenching in the proximity of second phase particles and corrosion products. Addition of 2-MBT into the corrosive environment results in excellent corrosion inhibition, with the alloy matrix and the second phase particles appearing uncorroded (Fig. 11). The EDX spectra reveal the following elemental weight percentages: from point A in Fig. 11: C: 23.6, Al: 33.7, Mn: 3.0, Fe: 11.2, Cu: 28.5 and from point B, C: 14.3, Al: 38.9, Mn: 6.3, Fe: 10.7, Cu: 13.8 indicating that the Al–Cu–Fe–Mn particles are uncorroded.

The EDX spectrum from the S-phase particle (point C) displays the weight percentages: C: 17.8, Mg: 11.8, Al: 29.2 and Cu: 41.3 indicating that the particle is also uncorroded.

In the presence of BTZ, the surface appears smoother compared with the specimen without inhibitor. However, a number of second phase particles have been removed from the surface (Fig. 12). Figure 12 presents a corroded intermetallic particle with corrosion.

**Surface morphology**

The surface morphology of AA 2024-T3 after immersion in 3.5% NaCl solution with and without inhibitors was examined by SEM. Figure 10 shows an image of AA 2024-T3 after 6h immersion in 3.5% NaCl, revealing trenching in the proximity of second phase particles and corrosion products. Addition of 2-MBT into the corrosive environment results in excellent corrosion inhibition, with the alloy matrix and the second phase particles appearing uncorroded (Fig. 11). The EDX spectra reveal the following elemental weight percentages: from point A in Fig. 11: C: 23.6, Al: 33.7, Mn: 3.0, Fe: 11.2, Cu: 28.5 and from point B, C: 14.3, Al: 38.9, Mn: 6.3, Fe: 10.7, Cu: 13.8 indicating that the Al–Cu–Fe–Mn particles are uncorroded. The EDX spectrum from the S-phase particle (point C) displays the weight percentages: C: 17.8, Mg: 11.8, Al: 29.2 and Cu: 41.3 indicating that the particle is also uncorroded.

In the presence of BTZ, the surface appears smoother compared with the specimen without inhibitor. However, a number of second phase particles have been removed from the surface (Fig. 12). Figure 12 presents a corroded intermetallic particle with corrosion.

**Table 2.** The extrapolated values of $\beta_c$, $\beta_a$, B, $E_{corr}$ and $i_{corr}$ form the potentiodynamic polarization curves form in Fig. 9

| Potentiodynamic polarization | No inhibitor | 2-MBT | BTZ | 8-HQ |
|-----------------------------|--------------|-------|-----|------|
| $E_{corr}$ (V vs SCE)       |              |       |     |      |
| $i_{corr}$ (μA cm$^{-2}$)   |              |       |     |      |
| $\beta_c$ (V)               |              |       |     |      |
| $\beta_a$ (V)               |              |       |     |      |
| B                           |              |       |     |      |
| EN                           |              |       |     |      |
| $R_{total}$ (Ω cm$^2$)      | 11135        | 67260 | 23745 | 13358 |
| $i_{corr}$ ($B / R_{total}$) (μA cm$^{-2}$) | 2.36 | 0.69 | 1.94 | 3.68 |
| $R_{in}$ (24 h) (Ω cm$^2$)  | 15859        | 78964 | 26984 | 9130 |
| $i_{corr}$ ($B / R_{in}$)   (μA cm$^{-2}$) | 1.66 | 0.588 | 1.7 | 5.4 |

2-MBT, 2-mercaptobenzothiazole; BTZ, benzotriazole; 8-HQ, 8-hydroxyquinoline; EIS, electrochemical impedance spectroscopy; EN, electrochemical noise.
products nearby, as evident from the elemental weight percentages from the EDX spectrum: C: 14.4, O: 18.6, Mg: 0.8, Al: 61.4 and Cu: 4.9. In Fig. 12, a surface film, likely to be because of the deposition of BT on the alloy matrix, is evident. The surface of the alloy after corrosion in the presence of 8-HQ reveals frequent trenching and cavities that resulted from the removal of second phase particles, suggesting poor corrosion protection properties [Figs. 13(a)-(c)]. In Fig. 13(b) and (c), a corroded S-phase particle with corrosion products is presented with elemental weight percentages from the EDX measurement: C: 39.8, O: 12.1, Mg: 0.6, Al: 39.3, Cu: 43.9 and Cl: 1.1.

Figure 10. Scanning electron micrograph of the surface of AA 2024-T3 after 6 h of immersion in 3.5% NaCl, showing trenching in the proximity of second phase particles.

Figure 11. Scanning electron micrographs of the surface of AA 2024-T3 after 24 h immersion in 3.5% NaCl with 2-MBT, displaying second phase particles. The arrows indicate the locations where the energy dispersive X-ray spectra were taken.

Figure 12. Scanning electron micrograph of the surface of AA 2024-T3 after 6 h immersion in 3.5% NaCl with 5 mM benzotriazole, showing corrosion attack on an intermetallic particle. The arrow indicates the location where the energy dispersive X-ray spectrum was taken.

Figure 13. (a), (b) Secondary electron micrographs and (c) back scattered micrograph of the surface of AA 2024-T3 after 6 h immersion in 3.5% NaCl with 8-hydroxyquinoline, displaying corrosion attack on an S-phase particle. The arrow indicates the location where the energy dispersive X-ray spectrum was taken.
Discussion

According to the electrochemical techniques employed in this work, 2-MBT provides excellent anti-corrosive properties to AA 2024-T3 substrates in 3.5% NaCl solution. EN measurements presented high noise resistance values after 24 h of immersion testing (79 kΩ cm²) compared with the specimen immersed in the absence of the inhibitor (15.9 kΩ cm²). Similar resistance values obtained from EIS measurements supported the EN results. The fitted EIS data presented total resistance values of 67.3 and 11.1 kΩ cm² in the case of 2-MBT and the specimen without inhibitor, respectively. Potentiodynamic polarization curves and the split cell technique showed that 2-MBT decreases both the anodic and cathodic reaction rates with corrosion current density values of 1.34 × 10⁻⁷ A cm⁻² being 1 order of magnitude lower than the specimen without inhibitor (6.85 × 10⁻⁶ A cm⁻²). The corrosion current density values obtained from EN and EIS measurements were 5.89 × 10⁻⁷ and 6.9 × 10⁻⁷ A cm⁻², respectively, in the case of 2-MBT, and in the case of the specimen without inhibitor the values were 1.66 × 10⁻⁶ and 2.36 × 10⁻⁶ A cm⁻², respectively. The effect of 2-MBT on the cathodic current density of AA 2024-T3 in the polarization curves can be explained by the formation of a film over the cathodically active Cu-rich particles as suggested in Marconato et al.12 and Ohsawa and Seutaka13. The reduction of the anodic current density might be related to the formation of a protective film above the alloy matrix.

Addition of BTZ presented decreased anodic current densities, while the cathodic current densities are close to the specimen without inhibitor, as suggested by polarization curves and the split cell technique. Therefore, the noise resistance values (27 kΩ cm²) and the polarization resistance (9.16 kΩ cm²) are higher than the specimen without inhibitor (15.9 and 1.26 kΩ cm², respectively), but lower than the specimen immersed with 2-MBT (79 and 31.8 kΩ cm², respectively). It has been suggested that BTZ is an effective corrosion inhibitor for copper18 because it forms a film on the metal surface because of the affinity between the triazole ring and the copper oxides.19 On an aluminium alloy, copper enriches at the surface following selective oxidation of aluminium, and it is possible that a film displaying some protective properties might form on the aluminium–copper alloy. As a result, some reduction in the anodic current during potentiodynamic polarization is observed. On the other hand, AA 2024-T3 in the presence of 8-HQ presents anodic and cathodic current densities close to the values for the specimen in the absence of the inhibitor as observed by the polarization curves and the split the cell technique. As expected, the noise resistance (9.13 kΩ cm²) and the polarization resistance (1.58 kΩ cm²) are very close to the values of the specimen without inhibitor. The inhibition effect of 8-HQ on AA 2024-T3 in 0.05 M NaCl solution, which was observed in Ohsawa and Seutaka, is not evident when the chloride concentration is increased to 3.5% wt. It should be noted that the structural difference between the tested inhibitors is that only 2-MBT contains thiol groups. Conversely, 8-HQ has a hydroxyl and a tertiary amino group and BTZ has a secondary and two tertiary amino groups. The findings presented here are in agreement with the suggestions of Harvey et al.20 that inhibitors with thiol and amino groups are more effective compared with inhibitors with hydroxyl groups for the AA 2024-T3.

It can be concluded that only 2-MBT presents a strong effect on the inhibition of both the anodic and the cathodic reaction rates as evident from the polarization curves and the split cell technique. On the other hand, BTZ affects only the anodic reaction rate, and 8-HQ does not provide significant inhibition, as evident from the values of anodic and cathodic current densities measured during potentiodynamic polarization that are similar to the specimen immersed in the solution without inhibitor. The mixed inhibitor effect of 2-MBT results in the most effective long-term protection, as evident from the high values of noise resistance maintained for over 400 h and the uncorroded appearance of the alloy surface.

Conclusions

Among the tested inhibitors, 2-MBT provides excellent corrosion inhibition properties to AA 2024-T3 substrates, with the noise resistance maintaining high values for over 400 h of immersion and the high low-frequency impedance values in 3.5% NaCl solution. Conversely, BTZ and 8-HQ presented values of noise resistance and impedance at the low frequency range close to the specimen immersed in the absence of the inhibitor. Moreover, potentiodynamic polarization tests and the split cell technique suggest that the 2-MBT inhibitor decreases the rate of both the anodic and the cathodic reactions. BTZ decreases only the anodic reaction rate and the addition of 8-HQ presents anodic and cathodic current densities values similar to the specimen corroding in the absence of inhibitor. SEM micrographs and EDX measurements complement the electrochemical results. Overall, the data suggest that 2-MBT provides excellent corrosion protection properties to AA 2024-T3 in demanding environments.

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References

[1] J. D. Zhang, S. K. Li, J. Occup. Environ. Med. 1997, 39, 315.
[2] M. Costa, C. B. Klein, Crit. Rev. Toxicol. 2006, 36, 155.
[3] S. V. Lamaka, M. L. Zheludkevich, K. A. Yasakau, M. F. Montemor, M. G. S. Ferreira, Electrochim. Acta 2007, 52, 7231.
[4] L. Tommasani, G. Brunoro, A. Frignani, C. Monticelli, M. Dal Colle, Corros. Sci. 1997, 39, 1221.
[5] K. Es-Salah, M. Keddam, K. Rahmouni, A. Shiri, H. Takenouti, Electrochim. Acta 2004, 49, 2771.
[6] A. Naguib, F. Mansfeld, Corros. Sci. 2001, 43, 2147.
[7] A. N. Khramov, N. N. Voedvin, V. N. Balbyتسhev, M. S. Donley, Thin Solid Films 2004, 447/448, 549.
[8] H. Yang, W. J. van Ooij, Proc. Org. Coat. 2004, 50, 149.
[9] B. Trachli, M. Keddam, H. Takenouti, A. Shiri, Proc. Org. Coat. 2002, 44, 17.
[10] M. L. Zheludkevich, K. A. Yasakau, S. K. Poznyak, M. G. S. Ferreira, Corros. Sci. 2005, 47, 3368.
[11] D. G. Shchukin, S. V. Lamaka, K. A. Yasakau, M. L. Zheludkevich, M. G. S. Ferreira, H. Mohwald, J. Phys. Chem. C 2008, 112, 958.
[12] J. C. Marconato, L. O. Bulhoes, M. L. Temperini, Electrochim. Acta 1997, 43, 771.
[13] M. Ohsawa, W. Seutaka, Corros. Sci. 1979, 19, 709.
[14] E. M. Sheer, S.-M. Park, Electrochim. Acta 2006, 51, 6556.
[15] L. Garrigos, N. Pibe, F. Dabosi, Electrochim. Acta 1996, 41, 1209.
[16] G. P. Ciccileo, B. M. Rosales, F. E. Varela, J. R. Vilche, Corros. Sci. 1998, 40, 1915.
[17] G. Moretti, V. V. Molokanov, G. Quartarone, A. Zingales, Corrosion 1998, 54, 135.
[18] M. Metikos-Hukovic, R. Babin, A. Marinovic, J. Electrochem. Soc. 1998, 145, 4045.
[19] O. Holander, R. C. May, Corrosion 1985, 41, 39.
[20] R. J. Chin, D. Altura, K. Nobe, Corrosion 1973, 29, 472.
[21] F. E.T. Heakal, S. Haruyama, Corros. Sci. 1980, 20, 887.
[22] S. V. Lamaka, M. L. Zheludkevich, K. A. Yasakau, M. F. Montemor, P. Cecilio, M. G. S. Ferreira, Electrochim. Commun. 2006, 8, 421.
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[23] D. Shchukin, M. Zheludkevich, K. Yasakau, S. Lamaka, M. G. S. Ferreira, H. Mohwald, *Adv. Mater.* 2006, 18, 1672.
[24] N. C. Rosero-Navarro, M. Curioni, R. Bingham, A. Duran, M. Aparicio, R. A. Cottis, G. E. Thompson, *Corros. Sci.* 2010, 52, 3356.
[25] M. Curioni, A. C. Balaskas, G. E. Thompson, *Corros. Sci.* 2013, 77, 281.
[26] C. Monticelli, G. Brunoro, A. Frignani, G. Trabanelli, *J. Electrochem. Soc.* 1992, 139, 706.
[27] W. Qafsaoui, F. Huet, H. Takenouti, *J. Electrochem. Soc.* 2009, 156, C67.
[28] A. C. Balaskas, M. Curioni, G. E. Thompson, *J. Electrochem. Soc.* 2014, 161, C389.
[29] M. Iannuzzi, J. Kovac, G. S. Frankel, *Electrochim. Acta* 2007, 52, 4032.
[30] W. J. Clark, J. D. Ramsey, R. L. McCreery, G. S. Frankel, *J. Electrochem. Soc.* 2002, 149, B179.
[31] M. I. Jafar, J. L. Dawson, D. G. John, *Electrochemical Impedance and Harmonic Analysis Measurements on Steel in Concrete, Electrochemical Impedance: Analysis and Interpretation, ASTM STP 1188* (Eds: J. R. Scully, D. C. Silverman, M. W. Kendig), American Society for Testing and Materials, Philadelphia, 1993, pp. 384–403.
[32] T. G. Harvey, S. G. Hardin, A. E. Hughes, T. H. Muster, P. A. White, T. A. Markley, P. A. Corrigan, J. Mardel, S. J. Garcia, J. M. C. Mol, A. M. Glenn, *Corros. Sci.* 2011, 53, 2184.