Electrochemical evaluation myclobutanil as inhibitor for copper in nitric acid medium

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Abstract. Myclobutanil is a triazole fungicide with low toxicity and easily biodegradable so that it can be used as an alternative corrosion inhibitor in metal pickling. Myclobutanil was studied as a corrosion inhibitor of Cu in 0.5M HNO3 solutions by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). Electrochemical test show that myclobutanil is an effective inhibitor and the inhibition efficiency equal approximately to 93.7% when the inhibitor concentrations were fixed in 1mM.

1. Introduction
Copper and its alloys are exceedingly sensitive to corrosion in strong acidic media such as sulfuric acid and nitric acid. [1] The most effective and pragmatic one is employing organic inhibitors to eliminate the destructive chemical attack of metal. [2] Traditional compounds such as Benzotriazole (BTA) and its derivatives have caused serious environmental problem due to their environmental harmful characteristics and biological toxicity. [3] Myclobutanil is a vital triazole fungicide extensively adopted to control powdery scab and powdery mildews in plants by processing leaves and seeds. [4,5] Myclobutanil is an attractive material as eco-friendly corrosion inhibitors because of its characteristics such as low toxicity, cheap, and has no permanent adverse effects on the environment. Li and his coworkers confirm that myclobutanil is an effective corrosion inhibitor for copper in 3.5% NaCl solution. [5] No work regarding myclobutanil as inhibitor for copper in nitric acid medium has been published till now. Therefore, Myclobutanil as an environmentally friendly inhibitor for copper in nitric acid solution was evaluated by electrochemical and SEM.

Figure 1. The chemical structures of the myclobutanil.
2. Materials and preparation

The HNO₃ solution were prepared from the analytical reagent grade nitric acid and deionized water. The studied inhibitors concentration of myclobutanil in the range from $1.0 \times 10^{-5}$ to $1.0 \times 10^{-3}$ M. The solution without myclobutanil was used for contrast. The chemical structures of the myclobutanil as shown in Figure 1. Electrochemical experiments were carried out in CHI760E Work Station with a three-electrode glass cell, the pure copper as working electrode (WE) with the geometric surface area of 0.785 cm². A saturated mercurous sulfate electrode (SMSE) as a reference electrode. A platinum foil (10 cm²) as the counter electrode. An aqueous thermostat to control the test temperature. For more electrochemical testing methods, see reference to RSC Adv., 2020, 10, 21517. [6] Copper specimens (purity, 99.99%, 2.0×1.0×1.0 cm) for SEM.

3. Results and discussion

3.1 Electrochemical test

The polarization curves for copper in 0.5 M nitric acid with and without different concentrations of myclobutanil at 288,298,308,318K are presented in Figure 2. Electrochemical parameters including $I_{corr}$, $E_{corr}$, anodic and cathodic Tafel slopes ($\beta_a$, $\beta_c$) acquired from the polarization curves at various temperatures are summarized in Table 1. The inhibitive efficiency can be calculated from Eq. (1). [6]

$$I_{corr\%} = \frac{I_{corr} - I_{corr\ (inh)}}{I_{corr}} \times 100$$ (1)

Where $I_{corr}$ is the corrosion current density without myclobutanil and $I_{corr\ (inh)}$ is the corrosion current density with different concentrations of myclobutanil in 0.5 M nitric acid, respectively.

As shown in Figure 2 and Table 1, both the anodic and cathodic parts of polarization curves were effected with the increase of myclobutanil inhibitors added to solution. With increasing the concentration of myclobutanil, the maximum inhibition efficiencies reached about 93.7% at $10^{-3}$M, 298K, the results present a positive efficient inhibition capability of myclobutanil at high concentrations. The values of $I_{corr}$ rises with increasing temperature as shown in Table 1, which could be attributed to the adsorption equilibrium shifted towards the adsorption process, leading to a higher coverage on the copper surface.

| Temperature (K) | Concentration (M) | $E_{corr}$ (mV vs. SMSE) | $\beta_c$ (mV dec⁻¹) | $\beta_a$ (mV dec⁻¹) | $I_{corr}$ (μA cm⁻²) | $I_{corr\%}$ |
|----------------|------------------|-------------------------|------------------|------------------|-----------------|-------------|
| 288            | blank            | -39                     | 63.3             | 53.6             | 22.9            | --          |
|                | $1.0 \times 10^{-5}$ | -86                     | 205.1            | 75.2             | 17.8            | 22.3        |
|                | $3.2 \times 10^{-5}$ | -94                     | 194.7            | 312.5            | 12.2            | 46.7        |
|                | $1.0 \times 10^{-4}$ | -104                    | 180.1            | 40.5             | 4.7             | 79.5        |
|                | $3.2 \times 10^{-4}$ | -53                     | 137.5            | 87.3             | 2.2             | 90.2        |
|                | $1.0 \times 10^{-3}$ | -37                     | 130.3            | 102.5            | 2.1             | 90.8        |
| 298            | blank            | -3                      | 103.5            | 51.0             | 20              | --          |
|                | $1.0 \times 10^{-5}$ | -40                     | 281.4            | 43.3             | 6.7             | 66.5        |
|                | $3.2 \times 10^{-5}$ | -58                     | 241.8            | 52.9             | 6.1             | 69.5        |
|                | $1.0 \times 10^{-4}$ | -54                     | 202.3            | 79.7             | 5.7             | 71.5        |
|                | $3.2 \times 10^{-4}$ | -68                     | 198.8            | 53.8             | 3.86            | 80.7        |
|                | $1.0 \times 10^{-3}$ | -38                     | 199.3            | 155.0            | 1.26            | 93.7        |

|                | blank            | -33                     | 78.8             | 55.5             | 61              | --          |
|                | $1.0 \times 10^{-5}$ | -54                     | 225.9            | 53.9             | 46              | 44.3        |
The EIS plot in Nyquist format with and without of myclobutanil in nitric acid at 288,298,308,318K is shown in Figure 3. EIS shows a depressed capacitive loop, the diameter of the semicircle increases with concentrations of myclobutanil and reach maximum at $10^{-3}$ M. The Nyquist plot were fitted using the circuit model as shown Figure 4. $R_s$ represents the solution resistance, $R_f$ represents the film resistance of copper, and $R_{ct}$ is the charge-transfer resistance. CPE$_f$ and CPE$_dl$ are the constant phase angle elements (CPE), which modelling the capacitance of protective film $C_f$ and the electrical double-layer $C_{dl}$, respectively. Figure 5 shows the fitted Nyquist, Bode Phase and phase angle plots of copper in nitric acid solution without or with different concentrations of myclobutanil at 298K, respectively. It can be seen from the Figure 5b that Bode and phase angle plots refer to the presence of an equivalent circuit which contains a two time constant phase element in the metal/solution interface [7].

| Concentration | Log(i/Acm$^{-2}$) | Value | Log(i/Acm$^{-2}$) | Value |
|---------------|-------------------|-------|-------------------|-------|
| 3.2×10$^{-5}$ | -107              | 355.7 | 84.4              | 34    |
| 1.0×10$^{-4}$ | -110              | 171.2 | 179.3             | 29    |
| 3.2×10$^{-4}$ | -112              | 265.6 | 189.4             | 14    |
| 1.0×10$^{-3}$ | -111              | 259.9 | 213.8             | 5.7   |
| blank         | -93               | 105.8 | 9.5               | 400   |
| 1.0×10$^{-5}$ | -104              | 142.3 | 117.7             | 170   |
| 3.2×10$^{-5}$ | -94               | 187.2 | 81.9              | 97    |
| 1.0×10$^{-4}$ | -94               | 167.8 | 112.3             | 44    |
| 3.2×10$^{-4}$ | -60               | 157.3 | 230.7             | 40    |
| 1.0×10$^{-3}$ | -49               | 346.4 | 383.6             | 35    |

**Figure 2.** The polarization curves for copper in acid solution with the different concentrations of myclobutanil: (a) 288, (b) 298, (c) 308, (d) 318K
The electrochemical impedance parameters are shown in Table 2. The charge transfer resistance obtained from EIS measurements were used to calculate the inhibitor efficiency according to the following equation: [7]

\[ I_{EZ\%} = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100 \]  

(2)

Where \( R_{ct} \) and \( R_{ct}^0 \) stand for the charge transfer resistance values with and without myclobutanil, respectively.

| Temperature (K) | Concentration (M) | \( R_0 \) (Ω cm²) | \( C_f \) (µF/cm²) | \( n_1 \) | \( R_f \) (Ω cm²) | \( Q_{dl} \) (µF/cm²) | \( n_2 \) | \( R_{ct} \) (kΩ cm²) | \( I_{EZ\%} \) |
|-----------------|------------------|-----------------|-----------------|--------|-----------------|-----------------|--------|-----------------|----------------|
| 288             | blank            | 1.64            | 78.4            | 0.87   | 200.6           | 2576            | 0.36   | 0.489           | --             |
|                 | 1.0×10⁻⁵         | 1.96            | 9.5             | 0.92   | 100.5           | 118.6           | 0.64   | 2.189           | 77.7           |
|                 | 3.2×10⁻⁵         | 1.91            | 14.5            | 0.90   | 178.2           | 91.5            | 0.87   | 2.698           | 81.9           |
|                 | 1.0×10⁻⁴         | 1.50            | 21.2            | 0.91   | 83.0            | 131.4           | 0.62   | 2.954           | 83.4           |

Figure 3. Nyquist plots of copper in 0.5 M nitric acid with different concentrations of myclobutanil: (a) 288K, (b) 298K, (c) 308K and (d) 318K.

\( R_{ct} \) values increased with the increasing of myclobutanil as shown in Figure 3 and Table 2, while the \( C_{dl} \) values decreased. \( R_{ct} \) value of the blank electrode is about 359 Ω cm², while the \( R_{ct} \) of copper in nitric acid with various concentrations of myclobutanil at 298K was attained through the equivalent circuit technique as 1106, 1231, 1790, 4076 and 4683 Ω cm², respectively. The corresponding \( I_{EZ\%} \) values were calculated from the equation (2) as 67.5, 70.8, 79.9, 91.2 and 92.3 with myclobutanil at different concentrations, respectively. The \( I_{EZ\%} \) values obtained from the EIS study are in acceptable agreement with those obtained from potentiodynamic polarization study.
| Concentration | Zreal | Zimag | 0 | 200 | 400 | 600 | 800 | 0 | 200 | 400 | 600 | 800 |
|---------------|-------|-------|---|-----|-----|-----|-----|---|-----|-----|-----|-----|
| 3.2×10⁻⁴ M   | 1.77  | 19.9  | 0.91| 47.0 | 114.4| 0.64 | 3.605| 86.4|
| 1.0×10⁻³ M   | 1.96  | 18.5  | 0.90| 37.1 | 78.6 | 0.78 | 5.231| 90.6|
| 1.0×10⁻⁵ M   | blank | 1.78  | 125.3| 0.85| 74.6 | 1084 | 0.42 | 0.359|--|
| 298 | 3.2×10⁻⁵ M | 1.72 | 15.8 | 0.80| 19.9 | 303.5 | 0.80| 1.106|67.5|
| 1.0×10⁻⁴ M   | 1.20  | 9.4   | 1.00| 17.6 | 242.6| 0.56 | 1.231|70.8|
| 308 | 1.0×10⁻⁴ M | 1.11 | 41.9 | 0.83| 41.9 | 225.3| 0.77 | 1.790|79.9|
| 3.2×10⁻⁴ M   | 1.43  | 9.5   | 0.89| 35.9 | 77.3 | 0.80 | 4.076|91.2|
| 1.0×10⁻³ M   | 0.87  | 10.7  | 0.83| 14.9 | 40.4 | 0.81 | 4.683|92.3|
| 1.0×10⁻⁵ M   | blank | 1.19  | 456.1| 0.84| 141.0| 184.2| 0.84| 0.067|--|
| 308 | 1.0×10⁻⁵ M | 1.12 | 299.4| 0.81| 34.9 | 145.3| 0.81| 0.201|66.7|
| 3.2×10⁻⁵ M   | 1.18  | 243.4 | 0.78| 53.3 | 91.1 | 0.93 | 0.711|90.6|
| 1.0×10⁻⁴ M   | 1.08  | 32.8  | 0.92| 120.8| 243.1| 0.84 | 0.943|92.9|
| 3.2×10⁻⁴ M   | 1.14  | 21.9  | 0.88| 44.7 | 161.6| 0.84 | 1.476|95.5|
| 1.0×10⁻³ M   | 0.88  | 10.7  | 0.86| 85.5 | 65.4 | 0.83 | 2.402|97.2|
| 318 | blank | 1.24  | 109.4| 0.79| 42.2 | 310.6| 0.82| 0.021|--|
| 1.0×10⁻⁵ M   | 1.33  | 76.8  | 0.78| 107.6| 323.1| 0.79 | 0.040|47.5|
| 3.2×10⁻⁵ M   | 1.19  | 55.6  | 0.72| 310.5| 128.2| 1.0  | 0.064|67.1|
| 1.0×10⁻⁴ M   | 1.17  | 185.0 | 0.84| 94.9 | 27.7 | 0.90 | 0.158|86.7|
| 3.2×10⁻⁴ M   | 1.24  | 37.9  | 0.94| 19.5 | 61.5 | 0.82 | 0.475|95.6|
| 1.0×10⁻³ M   | 0.97  | 12.4  | 0.87| 49.4 | 106.1| 0.83 | 1.272|98.3|

Figure 4. Equivalent circuits used to fit the EIS data.

Figure 5. Nyquist (a) and Bode (b) plots of copper obtained in 0.5 M nitric acid and containing 0, 10⁻⁵, 3.2×10⁻⁵ and 3.2×10⁻⁴ M myclobutanil at 298 K (Solid lines show fitted results).
3.2 SEM
SEM images of bronze sample before and after immersed in nitric acid in the absence and presence of 10⁻³ M myclobutanil for 8 h at 298K are shown in Figure 6. The SEM image of the freshly abraded copper was also given in Figure 6a for comparison. The images given in Figure 6b revealed that the surface of sample in the absence of the myclobutanil is severely corroded. The copper specimen is well protected and much less corroded area on the surface as shown in Figure 6c. From these micrographs it can be concluded that corrosion of copper can be inhibited by the inhibitor of myclobutanil.

Figure 6. SEM morphology of Cu immersed in 0.5 M nitric acid for 8 h at 298K, polished Cu sample(a), without (b) and with 10⁻³ M myclobutanil (c).

4. Conclusion
The myclobutanil as Cu inhibitor in 0.5 M nitric acid was found to have a promising inhibition performance and its inhibition efficiency increases with the increase of myclobutanil and reaches a maximum of 92.3% at 298K at 10⁻³ M according to the EIS measurements. The inhibition efficiency obtained from the EIS study was in acceptable agreement with those obtained from potentiodynamic polarization study. SEM shown that corrosion of copper can be inhibited by the inhibitor of myclobutanil.

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