Effects of Myclobutanil on Copper Corrosion as a Corrosion Inhibitor in H$_2$SO$_4$ Solution

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Abstract. This paper discusses the investigation of myclobutanil, namely 1-(4-Chlorophenyl)-2-(hydro-1,2,4-triazole-1-methyl)-amylecyanide as a inhibitor for copper corrosion in the acidic solutions (with 0.5M H$_2$SO$_4$). Electrochemical impedan ce spectroscopy (EIS) and potentiodynamic polarization was used to investigate its inhibition efficiency. The result shows inhibition efficiency raises rapidly when the amount of myclobutanil’s additive increasing. In 0.5M H$_2$SO$_4$ solution, the maximal inhibition efficiency of myclobutanil re ached 89.4% at $10^{-3}$M. The analysis of Polarization curves also indicates that myclobutanil is one kind of mixed-type inhibitor. The results of potentiodynamic polarization measurements increase the confidence of the results obtained from EIS measurements.

1. Introduction
Copper has wide application in electronic products because its good thermal conductivity and electrical property. Nevertheless, copper is prone to corrosion in acidic solutions for a long time. Corrosion inhibitor is easiest and cheapest means to reduce the metal materials’ corrosion in strong electrolyte[1]. Therefore, it is necessary to find highly efficient and profitable inhibitors instead of harmful and expensive inhibitors to inhibit copper corrosion in acidic solutions. Fortunately, myclobuntin as an agricultural chemical has volume production, lower prices and it is ecologically friendly. In this work, the corrosion behavior of copper in acidic solutions with different concentration of myclobutanil was invested by potentiodynamic polarization curve tests and EIS measurements.

2. Materials And Methods

2.1. Materials
The pure copper rod (99.99%) was used as the working electrode (WE) in this experiment. Copper rod is wrapped in epoxy resin, and its exposed surface area is 0.785cm$^2$. The working electrode was polished by sandpaper from 800 to 2400 grits, then washed it with acetone and ethanol. Before using working electrode, rinsed it with deionized water.

Diluting analytical grade sulfuric acid with deionized water, the corrosion solution used in this essay was prepared, which contained 0.5M H$_2$SO$_4$. 
Myclobutanil's molecular structure is shown in figure 1. The different addition amount of the inhibitor is from $1 \times 10^{-5}$M to $1 \times 10^{-3}$M in 0.5M H$_2$SO$_4$ solution. The temperature was controlled to 298 K ($\pm$1 K) by means of a constant temperature water bath.

![Figure 1. The molecular structure of myclobutanil.](image)

2.2. Electrochemical Experiment

The electrochemical parameters were measured by a CHI760E electrochemical system by using a three-electrode cell in this paper. The auxiliary electrode used platinum electrodes, and the reference electrode was acted by saturated mercurous sulfate electrode (SMSE). The auxiliary electrode, the reference electrode and the working electrode was placed into a 250 ml beaker with 150 mL acidic solution for 10 minutes. Then the open-circuit potential (OCP) was measured until its change less than 2 mV during 5 minutes to attain a steady value.

The span of alternating current’s frequency was between 100 kHz and 100 mHz, and the peak sine wave of 10 mV was used as the excitation signal in the measurements of EIS. By scanning the potential from -250 mV to +250 mV at a scanning rate of 1 mV/s, the polarization curve was obtained. And electrochemical software was used to collect and analyze the data.

3. Results And Discussion

3.1. Polarization Curves Test

From figure 2, we can see copper’s anodic and cathodic potentiodynamic polarization curves in the acidic solutions with different concentrations of myclobutanil at 298K. The electrochemical parameters including corrosion potential ($E_{\text{corr}}$), corrosion current density ($I_{\text{corr}}$), anodic and cathodic Tafel slopes ($\beta_a$, $\beta_c$) obtained from the polarization curves are listed in table 1. The inhibition efficiency ($\eta\%$) are calculated by equation (1)[1-3]:

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

where $I_{\text{corr}}$ is the corrosion current density in the absence of inhibitor in the acidic solutions. And $I_{\text{corr(inh)}}$ presence various concentrations of inhibitor in H$_2$SO$_4$ solutions.

| Concentration (M) | $E_{\text{corr}}$ (mV SMSE) | $I_{\text{corr}}$ (μA/cm$^2$) | $\beta_c$ (mV/dec) | $\beta_a$ (mV/dec) | $\eta\%$ |
|-------------------|----------------|----------------|----------------|----------------|----------|
| Blank             | -522           | 12.07          | 200.8          | 160.5          | /        |
| $10^{-5}$         | -539           | 9.13           | 166.9          | 342.3          | 24.4     |
| $3.2 \times 10^{-5}$ | -509         | 5.63           | 196.0          | 165.3          | 53.4     |
We can find that the corrosion current density rapidly declined when the concentration of corrosion inhibitor increased from table 1. It makes clear that the myclobutanil can reduce corrosion rate and the highest inhibition efficiency reached 89.4% in the H₂SO₄ solution with 10⁻³M myclobutanil. On account of the corrosion potential’s change is less than 85mV [4], myclobutanil is a kind of mixed type inhibitor.

![Figure 2. Copper’s polarization curves in the acidic solution with different concentrations of inhibitor at 298K.](image)

3.2. Electrochemical Impedance Spectroscope Test

Nyquist diagrams for the copper is showed in figure 3. Different curves represent diverse electrochemical performance of copper in the acidic solution with no inhibitor or different concentrations of inhibitor at 298 K. It shows the diameter of arcs increases when myclobutanil concentration raising. The result indicates that corrosion is inhibited and the impedance values increases compared with the blank solution.

In table 2, some different parameters are listed including charge-transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and f_{max} which are obtained from impedance measurements. At Harnyama and Tsuru’s suggestion, R_{ct} can be acquired from different impedance between lower and higher frequencies[5]. In order to obtain C_{dl}, the f_{max} is analysed. C_{dl} values are calculated from the equation (2)[6]:

$$C_{dl} = \frac{1}{2\pi} \frac{1}{R_{ct} F_{max}}$$  (2)

where R_{ct} is the diameter of the loop, and F_{max} is the frequency at least impedance’s imaginary component.

The efficiencies of corrosion inhibitor η% with myclobutanil are calculated by equation (3)[7]:

| Concentration | 10⁻⁴ | 3.2×10⁻⁴ | 10⁻³ |
|---------------|------|---------|------|
| Current Density | -508 | -467   | -496 |
| Potential    | 1.86 | 1.67    | 1.28 |
| Resistance   | 209.8| 199.2   | 199.3|
| Efficiency   | 70.4 | 91.5    | 109.4|
| Efficiency   | 84.6 | 86.2    | 89.4 |
where $R_{ct}^0$ and $R_{ct}$ represents the resistance of charge transfer with no corrosion inhibitor and presence of inhibitor.

$$\eta\% = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100$$

(3)

Table 2 indicates that $R_{ct}$ values raise with the amount of inhibitor concentration increasing. The result shows that the inhibitor molecules form a protective film by adsorbing onto the copper surface, so then achieving the purpose of isolating copper and corrosive solution[8]. The maximum efficiency of inhibition arrived 82.0% in the acidic solution with $1 \times 10^{-3}$M myclobutanil. This result is consistent with the results of the polarization curve test.

Table 2. Electrochemical parameters calculated by copper’s impedance measurements in the acidic solution with diverse concentrations of inhibitor at 298K.

| Concentration (M) | $R_{ct}$ (Ω cm$^2$) | $F_{\text{max}}$ (Hz) | $C_{\text{dl}}$ (µF cm$^{-2}$) | $\eta\%$ |
|-------------------|----------------------|------------------------|-------------------------------|---------|
| Blank             | 4305.7               | 1.47                   | 25.15                         | /       |
| $1 \times 10^{-5}$| 8025.5               | 3.16                   | 6.28                          | 46.3    |
| $3.2 \times 10^{-5}$| 10547.8             | 1.47                   | 10.26                         | 59.2    |
| $1 \times 10^{-4}$| 15414.0              | 0.825                  | 12.52                         | 72.1    |
| $3.2 \times 10^{-4}$| 19363.1             | 0.147                  | 55.91                         | 77.8    |
| $1 \times 10^{-3}$| 23949.0              | 0.215                  | 30.91                         | 82.0    |

4. Conclusions
Myclobutanil was proved to have an assured effect in the copper’s corrosion at 298K in the solution with 0.5M H$_2$SO$_4$. Myclobutanil molecules decrease copper’s corrosion via adsorbing in the copper’s surface to form a protective film. Analysis of Polarization curves showed myclobutanil is a mixed-type inhibitor. The inhibition efficiency raises with the adding of the myclobutanil’s amount in
solution.

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