Adsorption Study of 2-mercaptobenzothiazole at Copper Surface as Corrosion Inhibitor in HCl

Taumy Alif Firman*, Yoki Yulizar

Abstract

Adsorption of 2-mercaptobenzothiazole (MBT) at copper surface has been studied to reduce the corrosion rate of copper in HCl solution 0.5 M. The adsorption data were fitted into Langmuir, Freundlich and Temkin isotherms. The results showed three different values of adsorption isotherm, the $R^2$ value of Langmuir isotherm model was the most linear, 0.9673. The maximum adsorption equilibrium constant of Langmuir isotherm model at copper surface was determined to be $2.33 \times 10^5$ L/mol using 50 ppm concentration of MBT at temperature 30 °C. Function of MBT at copper surface as corrosion inhibitor increases with the increase of inhibitor concentration. Analysis with ATR-IR spectrometry showed the adsorption type of MBT at copper surface as chemisorptions.

Keywords: Surface adsorption, 2-mercaptobenzothiazole, corrosion inhibitor, Copper, ATR-IR spectrometry.

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Introduction

Corrosion stands for material or metal deterioration or surface damage in an aggressive environment. Corrosion due to electrochemical reaction in which the metals transfer electrons to the environment and under goes a valence change from zero to a positive value. The environments are called electrolytes may be a liquid, gas or hybrid soil-liquid [1]. One of the most important metals but is often corrode is copper. Corrosion on copper can be treated with chemical method. The use of corrosion inhibitors is one method of chemical treatment using organic compounds that can protect the surface of copper from corrosion process due to the environment. The organic compounds such as triazole derivative [2], pyrazol derivative [3], and thiosemicarbazide [4] has been studied as corrosion inhibitor in acidic media. All the results of the study showed that the corrosion inhibitor compounds containing nitrogen and sulphur heterocyclic are the best % protection than another compounds without heterocyclic structure. One of the heterocyclic compounds containing sulphur and nitrogen in the aromatic ring is 2-mercaptobenzothiazole (MBT). In this research study the isotherm adsorption of MBT on the copper surface as a corrosion inhibitor with HCl 0.5 M as corrosion medium. The use of MBT, because having a heterocyclic structure and composed of the elements nitrogen and sulphur are capable of a lot expected adsorbed on a copper surface. Type evaluated whether the adsorption is formed following the Freundlich isotherm, Langmuir or Temkin.

Methodology

Materials.

Copper specimens from Good fellow (Cat. No. CV00320) used in weight loss measurement were mechanically cut into diameter 1.3 cm. The MBT chemical from Huang Yan ZheDong rubber Auxiliary Imp and Exp. Co, Ltd (CAS.No. 149-30-4). The HCl were used analytical grade.

Before measurement, the surface of copper was mechanically abraded with 350, 1000 and 1500 grades of emery paper, degreased with acetone, and rinsed by aquadest before each experiment.

The tests were performed in 0.5 M HCl solution containing various concentration of MBT (15-50 ppm). for each experiment, a freshly prepared solution was used.

Methods.

Copper specimens with diameter 1.3 cm, in triplicate, were immersed in 100 mL 0.5 M HCl solutions both in the absence and presence of the various concentration of the MBT for a period of 24 hours. The weight of specimens before and after immersion was determined. The inhibition efficiencies were evaluated using the formula...
\[
\text{Efficiency} (\%) = \left( \frac{W_{\text{corr}} - W_{\text{corr} \text{(inh)}}}{W_{\text{corr}}} \right) \times 100
\]

Where, \(W_{\text{ads}}\) weight loss of the sample in absence of the inhibitor and \(W_{\text{corr} \text{(inh)}}\) is weight loss of the sample in presence of the inhibitor.

The IR spectrum of the film formed on the surface of copper was recorded using ATR-IR spectrophotometer.

**Results and Discussions**

Efficiency of corrosion inhibitor depends on adsorption ability on surface metal. In this research, ability corrosion inhibitor to protect the metal from corrosion attack showed as a % efficiency.

![Figure 1](Image)

**Figure 1.** Effect of MBT concentration to inhibited corrosion process of copper in HCl 0.5 M with contact time 24 hours in temperature 30 °C

Figure 1 showed that % efficiency of copper corrosion was increase trend when the increased MBT concentration. Copper have high affinity to sulphur. When the increased MBT concentrations caused affect greater chance bonds formation between atoms sulphur from thiocarbonyl group (C=S) on MBT with copper to formed film layer. The % efficiency valuelinear with surface coverage. The surface coverage data obtained at different MBT concentration for the corrosion of copper in HCl 0.5 M is listed in Table 1.

The concentration data and surface coverage data can be used to analyse the isotherm adsorption mechanism. Most frequently used adsorption isotherms are the Langmuir, Freundlich and Temkin. The determination of whether to follow the adsorption isotherm Langmuir, Freundlich or Temkin done by plotting the concentration parameter and the parameter surface coverage at the chart with the various adsorption isotherm equation.[6]

\[
\text{Langmuir: } \frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C
\]

\[
\text{Freundlich: } \log \theta = \log K_{\text{ads}} + n \log C
\]

\[
\text{Temkin: } \frac{2aC}{2.303} = \log K_{\text{ads}} + \log C
\]

Where, \(C\) is the inhibitor concentration, \(\theta\) the surface coverage, \(K_{\text{ads}}\) the equilibrium constant of adsorption, \(a\) the molecular interaction parameter. The results data were plotted on Langmuir, Temkin and Freundlich adsorption isotherm to determine the type that occurs between MBT and copper surface as showed in Figure 2.

**Table 1.** Surface coverage for several MBT concentration

<table>
<thead>
<tr>
<th>Concentration of MBT (ppm)</th>
<th>Surface coverage (θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.0318</td>
</tr>
<tr>
<td>25</td>
<td>0.0848</td>
</tr>
<tr>
<td>35</td>
<td>0.1538</td>
</tr>
<tr>
<td>50</td>
<td>0.6310</td>
</tr>
</tbody>
</table>

Figure 2 showed that the adsorption of MBT on copper surface obeyed the Langmuir isothermal adsorption with \(R^2\) value of 0.9673. This means that MBT adsorbed by forming a layer on the copper surface. Based on this mechanism, the adsorption process is equivalent, and the ability of MBT to be bound copper surface is similar, does not depend on whether or not the copper surface occupied adjacent.[10]

Increase concentration of MBT to increase % efficiency MBT to protect copper from corrosion process. This effect can also be seen from increase value of the adsorption equilibrium constant, \(K_{\text{ads}}\). Value of \(K_{\text{ads}}\) showed stability between MBT on copper surface. From isotherm Langmuir can be determination of \(K_{\text{ads}}\) showed in Table 1.

**Table 2.** \(K_{\text{ads}}\) value in various concentration at temperature 30 °C

<table>
<thead>
<tr>
<th>No</th>
<th>Concentration of MBT (ppm)</th>
<th>(K_{\text{ads}}) (L mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>2.60 x 10(^3)</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>1.15 x 10(^4)</td>
</tr>
<tr>
<td>3</td>
<td>35</td>
<td>1.07 x 10(^4)</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>2.33 x 10(^4)</td>
</tr>
</tbody>
</table>

Effect of temperature causes irrelevance adsorption of MBT on copper surface.[7]. Increasing the temperature not only decreases \(K_{\text{ads}}\) but also increases the desorption process. Table 2 showed the effect temperature for value of \(K_{\text{ads}}\).
Interaction between MBT and copper were confirmed with characterization used ATR-IR spectrophotometer. The spectrum IR showed in Figure 3.

![Figure 3](image-url)

**Table 1.** Adsorption data for the adsorption of MBT on copper surface at different temperatures.

<table>
<thead>
<tr>
<th>No</th>
<th>Temperature (C)</th>
<th>$K_{ads}$ (L mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>$2.33 \times 10^5$</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>$1.07 \times 10^5$</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>$3.59 \times 10^4$</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>$6.04 \times 10^3$</td>
</tr>
</tbody>
</table>

The MBT can be used as corrosion inhibitor to protect copper from corrosion condition. The ability MBT for corrosion inhibitor showed from % efficiency to protect copper from the corrosion process. Adsorption of MBT in copper surface obeyed Langmuir isotherm.

**References**