Electrochemical and characterization surface investigations on the corrosion inhibition of copper by benzylsulfonamide in H$_2$SO$_4$ solution

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Abstract

The corrosion resistance of copper samples by benzylsulfonamide was evaluated by electrochemical and morphological approaches in 0.5 M H$_2$SO$_4$ solution. The Tafel curves demonstrated the mixed corrosion inhibition mechanism of the benzylsulfonamide on cooper surface in acidic medium. Electrochemical impedance spectroscopy (EIS) analysis results evidenced about corrosion inhibition efficiency of about 63% for the cooper sample subjected to the H$_2$SO$_4$ 0.5M. Also, the π-π*/n-π* electro-transitions in the benzylsulfonamide molecule in H$_2$SO$_4$ 0.5M were proved by the UV-Vis technique. The adsorption of benzylsulfonamide on copper surface obeys the Langmuir isotherm.

Keywords: Corrosion inhibition, Acid solution, EIS, adsorption isotherms, inhibitory efficiency.

1. Introduction

Corrosion is an unavoidable chemical/electrochemical interaction between metals and the aggressive environments, which can affect the mechanical properties of metals. This phenomenon is one of the most common problems in our daily life and in various industrial fields, such as the petrochemical industry, the machine and instrument industry, the transport of hydrocarbons and sewage plants.
Copper and its alloys are widely used in industry because of their remarkable physical and mechanical properties. Copper is a relatively noble metal; nevertheless, it can undergo severe corrosion in an aerated acidic environment or in environments containing chloride, sulfate, or nitrate ions [1, 2]. In order to obtain a shiny copper surface in certain areas of application, an H₂SO₄ pickling solution is often used to remove the oxidation film. However, the pickling reagent H₂SO₄ can damage the copper. The addition of corrosion inhibitors to the pickling liquid not only effectively reduces the corrosion of the copper substrate but also reduces sulfuric acid consumption [3, 4]. Furthermore, the study of copper corrosion inhibitors in H₂SO₄ solution has significant economic advantages [5]. Many organic compounds containing sulfur, phosphorus, nitrogen and oxygen atoms in their structure are effective inhibitors of copper corrosion in acidic media [6, 10]. Therefore, the development of compounds containing these functions as corrosion inhibitors has been of great interest. The effectiveness of an organic compound as an inhibitor depends mainly on its ability to be adsorbed on the metal surface. A large variety of organic compounds are known to be applicable as corrosion inhibitors in acidic media [11-14]. However, most of these compounds have been found to be toxic. The restrictions due to environmental protection require their replacement by new non-toxic or environmentally friendly compounds. For this reason, the development of non-toxic and biodegradable organic compounds as corrosion inhibitors has attracted a great deal of interest.

In this work, the study of the inhibitory properties of a synthesized molecule called benzylsulfonamide would be important in the context of the current priority to produce environmentally friendly inhibitors. The use of this compound at usual concentrations for corrosion inhibition has a negligible impact on human health and the environment. The benzylsulfonamide was synthesized and its structure was confirmed by different spectroscopic methods including: UV-vis, FTIR, ¹H NMR, and ¹³C NMR.

Then, the inhibition performance of benzylsulfonamide against copper corrosion in 0.5 M H₂SO₄ medium was exhaustively investigated by potentiodynamic polarization techniques; electrochemical impedance spectroscopy (EIS), and mass loss tests, thermodynamic study, and scanning electron microscopy (SEM) surface analysis.

2. Results and discussion

98 wt% sulfuric acid and ultrapure water were used to prepare 0.5M H₂SO₄ aggressive solution. The concentration of the inhibitor varied from 10⁻⁶ to 10⁻³ M. and the 0.5 M sulfuric acid solution without inhibitors taken as reference. The molecular structure of studied compound is presented in Figure 1 and the main characteristics of the synthesized compound are the following: Exact Mass: 186.05, Molecular Weight: 186.23, m/z: 186.05 (100.0%), 187.05 (8.6%), 188.04 (4.5%), Elemental Analysis: C, 45.15; H, 5.41; N, 15.04; O, 17.18; S, 17.22, Boiling Point: 681.83 [K], Log P: 0.6, Henry’s Law: 2.03, tPSA: 72.19, CLogP: 0.474, LogS: -1.594 [15].

![Figure 1. Molecular structure of benzylsulfonamide.](image-url)

2.1. Measurement of the potentiodynamic polarization

Tafel curves are shown in Figure 2 for cooper in H₂SO₄ 0.5 M solution in the absence and presence of the various concentrations of the test compound at 298 K. It can be obviously seen
that all cathodic and anodic curves move in the direction of low current densities with increasing concentrations of corrosion inhibitors. The corrosion potentials all moved in the positive direction with the increase of corrosion inhibition concentrations. In literature, it has been reported that [16, 17] if the displacement in $E_{\text{corr}}$ is $>85$ mV with respect to $E_{\text{corr}}$, the inhibitor can be seen as a cathodic or anodic type and 2) if the displacement in $E_{\text{corr}}$ is $<85$ mV, the inhibitor can be seen as mixed type. In our study, the maximum displacement in $E_{\text{corr}}$ value is 16.2 mV towards anodic region, which indicates that the benzylsulfonamid compound studied is mixed-type inhibitors [18]. In another aspect, all the branches of the cathode are almost parallel to each other, indicating that the mechanism of the cathodic reaction does not change with the addition of this compound. In the anode domain, when the polarization potential increases, all the anode branches corresponding to all the concentrations tested clearly show the desorption of the corrosion inhibitor molecule. This phenomenon is more marked for the highest concentration of this compound [19].

![Figure 2](image-url)

**Figure 2.** Tafel curves for copper in H$_2$SO$_4$0.5 M solution without and with different concentrations of the benzylsulfonamide compound at 298 K.

The electrochemical parameters obtained by extrapolating the Tafel lines, ($I_{\text{corr}}$), corrosion potential ($E_{\text{corr}}$), anodic Tafel slope ($b_a$), cathodic Tafel slope ($b_c$) and inhibition efficiency ($E$), are given in Table 1. The values of $E$ are obtained with the formula (1) as follows:

$$E (%) = (1 - \frac{I'_{\text{corr}}}{I_{\text{corr}}}) \times 100$$

Where $I'_{\text{corr}}$ and $I_{\text{corr}}$ denote for current densities of the working electrode in the 0.5 M H$_2$SO$_4$ without and with the investigated organics, respectively. As shown in Table 1.

It can be seen that the addition of the inhibitor leads to a decrease in corrosion current densities and, consequently, an increase in inhibitory efficiency values. Also, the inhibition efficiency values (E%) increase with the concentration of the inhibitor and reach a maximum value of 68.42% at 1 mM, indicating that the inhibition activity of the studied compound can be related to its adsorption on the copper surface forming a barrier preventing its dissolution.
**Tableau 1.** Electrochemical parameters obtained from polarization curves with and without inhibitor.

<table>
<thead>
<tr>
<th>[inhibiteur]M</th>
<th>$E_{corr}$(mV/ SCE)</th>
<th>$I_{corr}$(µA cm$^{-2}$)</th>
<th>$b_a$(mV/dec)</th>
<th>$b_c$(mV/dec)</th>
<th>$IE$ (%)</th>
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<td>43.3</td>
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<td>-81.7</td>
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</tr>
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<td>55.7</td>
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<td>1.20</td>
<td>67.1</td>
<td>-79.1</td>
<td>68.42</td>
</tr>
</tbody>
</table>

### 2.2. Results of the UV-Vis analysis

UV-vis spectroscopy is a powerful tool used to highlight the interaction between the metal and the inhibitors. UV-vis absorption spectra obtained from an H$_2$SO$_4$ 0.5M solution containing $10^{-3}$M benzylsulfonamide before and after 72 hours of immersion of the copper electrode at 25°C are shown in Figure 3. Three characteristic peaks were observed in the UV-Vis diagrams of the solution without copper electrodes. The obtained electronic absorption spectra show the bands in the UV-vis region with considerable charge transfer character owed to $\pi$- $\pi^*$ and n- $\pi^*$ transitions.

![Figure 3. UV-Vis spectrum of the H$_2$SO$_4$ 0.5 M solution with $10^{-3}$M of benzylsulfonamide before and after copper immersion.](image)

Obviously, the immersion of the copper electrode after 72 hours in the H$_2$SO$_4$ 0.5 M solution containing the inhibitor-induced the disappearance of the n - $\pi^*$ transition peak and the shift of the $\pi$ - $\pi^*$ transition peak; this is an indication of interactions between benzylsulfonamide inhibitor and copper surface [20].
2.3. Scanning electron microscopic analysis

In order to complete the results of the measurements obtained by electrochemical techniques a scanning electron microscopy analysis was used, to determine the morphology of the copper samples, after their immersion in the tested solution (H$_2$SO$_4$ 0.5 M) for 72 hours at room temperature, in the absence and presence of the inhibitor. We find that in the absence of an inhibitor (Figure 4(a)) that the sample surface is strongly corroded, on the other hand in the presence of 10$^{-3}$M of the organic molecule the sample surface becomes smoother (Figures 4(b)). This result indicates that a good protective adsorption film could be formed on the surface of the sample and that the corrosion of copper in 0.5M H$_2$SO$_4$ solution is remarkably inhibited by the inhibitor.

![Figure 4. SEM photographs of copper dipped in H$_2$SO$_4$ 0.5M](a) Without inhibitor and ((b) With inhibitor.)

2.4. Adsorption Isotherms

Basic information on the interaction between the inhibitor and the metal surface can be provided by the adsorption isotherm, which depends on the degree of electrode surface coverage ($\theta$). The plots of $C_{inh}/\theta$ against $C_{inh}$ for benzylsulfonamide give straight. The correlation coefficient of benzylsulfonamide is 0.9997 It is to say that their correlation coefficients are both greater than 0.95. This indicates that the benzylsulfonamide compound obeys the Langmuir adsorption isotherm on the copper in H$_2$SO$_4$ 0.5M.
3. Conclusion

The following conclusions can be reached from this study,
- The studied benzylsulfonamide compound exhibits a good inhibition action for copper corrosion in 0.5 M H₂SO₄ medium and its inhibition efficiency increases with increasing inhibitor concentration. The maximum value of the inhibition efficiency calculated is about 68.42% obtained at 10⁻³ M.
- The results obtained from the potentiodynamic polarization curves indicated that the studied compound acts as a mixed type inhibitor in H₂SO₄ 0.5 M.
- The UV-vis spectroscopic study revealed the existence of chemical interactions between benzylsulfonamide and copper.
- SEM observations confirmed the formation of a protective film by benzylsulfonamide on the copper surface.

References