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# Corrosion inhibition performance of 2-mercaptobenzimidazole and 2-mercaptobenzoxazole compounds for protection of mild steel in hydrochloric acid solution

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The effect of some mercapto functional azole compounds on the corrosion of mild steel in 1 M hydrochloric acid solution was studied by polarization and electrochemical impedance spectroscopy (EIS). Polarization studies showed depression of cathodic and anodic polarization curves in the presence of mercapto functional azole compounds, indicating mixed type corrosion inhibition of the compounds. Double layer capacitance and charge transfer resistance values were derived from EIS results. Changes in impedance parameters are indicative of adsorption of these compounds on the metal surface. Surface analysis SEM/EDX showing presence of sulfur on the surface confirmed the adsorption of the azole compounds on the mild steel surface as showed by electrochemical methods. Both compounds contain a pyridine-like nitrogen atom and a sulfur atom in their molecular structure, while they differ in only one heteroatom: oxygen in the oxazole ring and pyrrole-like nitrogen in the imidazole ring. The results of the electrochemical techniques revealed that changing the pyrrole like nitrogen atom to oxygen atom in the azole ring results in a decrease of corrosion inhibition performance in hydrochloric acid solution, which could be related to more negative charge on pyrrole-like nitrogen atom in comparison to oxygen atom as depicted by quantum chemical calculations.



## 1. Introduction

Hydrochloric acid solution is widely used as acid wash solution for removing rust and scale from the mild steel surface. However, the strong corrosivity of hydrochloric acid needs to be controlled by an appropriate corrosion inhibitor. Influence of some mercapto functional compounds including mercapto triazole derivatives [1], 2-aminophenyl-5-mercapto-1-oxa-3,4-diazole [2], 2-amino-5-mercapto-1,3,4-thiadiazole [3], 5-amino-3-mercapto-1,2,4-triazole [4], 4-salicylideneamino-3-phenyl-5-mercapto-1,2,4-triazole [5], 6-methyl-5-[m-nitro styryl]-3-mercapto-1,2,4-triazine [6], some mercapto oxadiazole derivatives [7] on corrosion of mild steel in hydrochloric acid solution have been studied with weight loss, polarization and EIS. The proposed mechanism of inhibition for the mentioned compounds in hydrochloric acid solution is adsorption on the mild steel surface. Some other mercapto functional compounds have been studied for corrosion inhibition in sulfuric acid solution like 1-methyl-5-mercapto-1,2,3,4-tetrazole [8], 4-amino-3-butyl-5-mercapto-1,2,4-triazole [9], 2-mercapto-5-methyl-1,3,4-thiadiazole [10], 2-mercaptobenzoimidazole, 5-mercapto-1-tetrazoleacetic sodium salt [11], 3-alkyl-4-amino-5-mercapto-1,2,4-triazole [12], 2-mercaptoimidazole [13].

Most of the mercapto functional azole compounds have shown mixed-type corrosion inhibition in acidic solutions for protection of mild steel [1–6,9–13], while there are some studies indicating that cathodic inhibition is predominant [7]. In acidic solutions, these compounds could be protonated. The protonated species may adsorb on the cathodic sites of the mild steel surface and decrease the evolution of hydrogen. Also, these compounds could adsorb on anodic sites through N and S atoms, heterocyclic and aromatic rings, which are electron donating groups.

This work intends to study inhibitive performance of 2-mercaptobenzimidazole and 2-mercaptobenzoxazole in hydrochloric acid solution using EIS in order to determine the effect of variation of pyrrole-like nitrogen in the imidazole ring to oxygen atom in the oxazole ring. In this regard, using quantum chemical calculations, it is tried to find out a correlation between quantum chemical parameters and inhibition efficiency obtained by electrochemical techniques.

Different calculation techniques are developed from pure mathematical to semiempirical methods. Density function theory (DFT)

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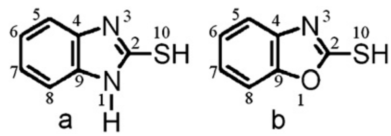


**Fig. 1.** The chemical structures of the compound used; MBI (a) and MBO (b).

**Table 1**
The composition of steel panels.

| Elements | wt% |
|---|---|
| C | 0.190 |
| Si | 0.288 |
| Mn | 1.390 |
| Cr | 0.026 |
| Mo | 0.018 |
| Co | 0.388 |
| Cu | 0.297 |
| Nb | 0.334 |

method based on Becke's hybrid exchange functional (B3) combined with the LYP correlation functional (B3LYP) has shown the best result, and it is widely used in literature [14–17]. Therefore, in this work DFT/B3LYP method is used.

## 2. Experimental

### 2.1. Material preparation

A laboratory grade hydrochloric acid solution was obtained from Merck to prepare 1 M HCl solution. Two mercapto functional azole compounds including 2-mercaptobenzimidazole (MBI) and 2-mercaptobenzoxazole (MBO) were obtained from Merck and used without further purification. The molecular structures of these compounds are shown in Fig. 1. The test solutions were prepared at four different concentrations of mercapto functional azole compounds ranging from 0.05 mM to 1 mM.

Mild steel panels with composition presented in Table 1 were polished using emery polishing paper 800 and then degreased using acetone.

### 2.2. Electrochemical studies

An area of 1 $cm^2$ of each sample was exposed to the electrolytes while other areas of the plate were sealed with beeswax-colophony mixture. EIS and polarization measurements were carried out using IVIUM COMPACTSTAT after 4 h immersion in test solutions at $25 \pm 1\,^{\circ}C$. EIS was implemented at open circuit potential within frequency range of $10^{-2}$ Hz to $10^{+4}$ Hz with 10 mV perturbation. After EIS examination, polarization was conducted at the rate of 2 mV/s from −250 mV to +250 mV of OCP (open circuit potential). Reference electrode and counter electrode were silver–silver chloride and graphite, respectively.

Throughout electrochemical test results, a 1 M HCl solution with no inhibitor was taken into consideration as Blank solution.

### 2.3. SEM–EDX studies

The surface of specimens after 4 h exposure to the 1 M HCl solution containing MBI and MBO were analyzed using SEM/EDX (Philips XL30).

### 2.4. Quantum chemical calculations

Quantum chemical calculations were performed using Gaussian 03W. B3LYP version of DFT was used with 6-311G basis set. Calculations were carried out on a PC computer equipped with AMD Athlon 64 X2 dual core processor 3800 and 1 GB RAM.

## 3. Results and discussion

### 3.1. Electrochemical measurements

Fig. 2 shows polarization curves for samples immersed in test solutions. It can be seen from the figure, increase of MBI and MBO concentrations from 0.05 mM to 1 mM resulted in depression of polarization curves. Both the anodic and cathodic current densities were decreased in Fig. 2 indicating that MBI and MBO suppressed both the anodic and cathodic reactions through adsorption on the mild steel surface. This suggests that MBI and MBO act as mixed-type corrosion inhibitor for mild steel in 1 M HCl solution. Corrosion

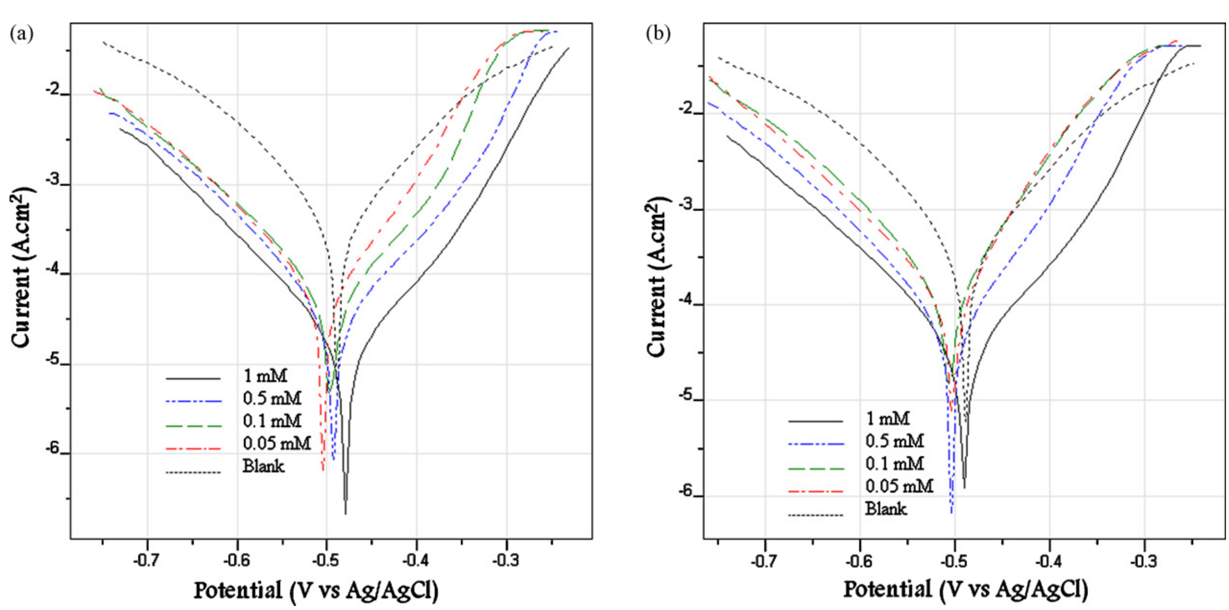


**Fig. 2.** Polarization diagram of mild steel at different concentration of MBI (a) and MBO (b) in 1 M HCl solution.