

New inhibitors for copper corrosion*

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Abstract: The study of the effectiveness of several potential copper corrosion inhibitors in acidic media was studied. The investigated thiazole derivative functional groups contain heterocyclic atoms such as nitrogen, sulfur, and oxygen. Thiazole derivatives, 5-benzylidene-2,4-dioxotetrahydro-1,3-thiazole (BDT) 5-(4'-isopropylbenzylidene)-2,4-dioxotetrahydro-1,3-thiazole (IPBDT), 5-(3'-thenylidene)-2,4-dioxotetrahydro-1,3-thiazole (TDT), and 5-(3',4'-dimethoxybenzylidene)-2,4-dioxotetrahydro-1,3-thiazole (MBDT) were tested for copper corrosion inhibition properties. The electrolyte solution was 0.1 M Na₂SO₄.

In situ information on corrosion and inhibition processes can be obtained using different techniques. Electrochemical measurements (EIS), *in situ* scanning probe microscopy (SPM), in addition to quartz crystal microbalance (QCM) measurements were applied. Those methods are very useful owing to their high sensitivity and resolution. Dynamic STM and AFM measurements on Cu(111) single-crystal electrode with and without the addition of some inhibitors were performed.

The presence of the isopropyl group in the case of IPBDT produced far better protection against copper corrosion in acidic sulfate-containing media than the rest of the derivatives.

INTRODUCTION

Copper is one of the most essential metals owing to its large industrial applications, such as electronics, etc. It is generally a relatively noble metal, however, it is susceptible to corrosion by acids and strong alkaline solutions, especially in the presence of oxygen or oxidants. In the pH range between 2 and 5, the dissolution of Cu is very rapid, and the formation of a stable surface oxide layer, which can passivate metal surfaces, is hindered. An oxide surface layer can only be formed in weak acid or alkaline solutions. The behavior of Cu in acidic media is extensively investigated, and several schemes have been presented for the dissolution process [1–5].

One of the most important methods in the corrosion protection of metals is the use of organic inhibitors to protect the metal surface from the corrosion environment.

The role of adsorption-type inhibitors can be explained by the Lewis acid-base interaction on metal surfaces. The molecular structure is one of the major factors that influence this interaction [2]. The molecular structure of thiazoles, tetrazoles contain atoms like N and S, which are easily able to bridge with other molecules [1,2,6–15]. For a metal such as copper, which can form multi-bonds, inhibitor molecules containing those atoms are strongly recommended.

Thiazole derivatives molecules adsorb probably through the sulfur atom or through coordination with the surface, forming a protective layer [16].

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Owing to stricter environmental regulations, low inhibitor toxicity is an important requirement for the applied inhibitors. The latest trend in industry is to replace toxic inhibitors, such as triazoles, with nontoxic organic chemicals that can cause no harm to the environment. In closed systems, thiazole derivatives can act as an excellent replacement for the toxic triazoles.

Previous studies have produced some promising results, showing that some thiazoles derivatives have excellent inhibition properties against copper corrosion [16]. The studied thiazole derivatives in this study are: 5-benzylidene-2,4-dioxotetrahydro-1,3-thiazole (BDT), 5-(4'-isopropylbenzylidene)-2,4-dioxotetrahydro-1,3-thiazole (IPBDT), 5-(3'-thenylidene)-2,4-dioxotetrahydro-1,3-thiazole (TDT), and 5-(3',4'-dimethoxybenzylidene)-2,4-dioxotetrahydro-1,3-thiazole (MBDT). These molecules have been studied on copper and cuprous oxide surfaces in an electrochemical environment.

Several investigations utilized quartz crystal microbalance (QCM) to investigate copper electrode behavior in acidic environment [11–17]. QCM is capable of detecting mass changes in the nanoscale range. It consists of piezoelectric quartz, with electrodes on both faces, inserted into a properly designed oscillator circuit. When a voltage is applied between the two faces, the crystal oscillates. The oscillation frequency of a quartz crystal is highly sensitive to the mass supported by the two faces of the device. When one face of the crystal is modified to function as the working electrode, changes of the electrode mass can be continuously monitored [18–19].

In situ STM and AFM were used to study processes at the solid/liquid interface at nanoscale. Local investigations of copper single-crystal electrode surfaces and the adsorption of those thiazole derivatives molecules on copper and cuprous oxide surfaces have been studied in an electrochemical environment.

The aim of this work was to investigate the adsorption and inhibition effect of different thiazole derivatives, on copper surface in acidic solution, and to analyze the dependence of polarization resistance and mass change in function of the type of the inhibitor molecule. The electrochemical behavior of copper and the inhibitor effectiveness were studied using electrochemical, electro-gravimetric, and surface analytical sensitive measurements.

EXPERIMENTAL

Electrodes

A polycrystalline Cu (99.99%) electrode was used for the electrochemical measurements. Electrochemically deposited copper layers were used for QCM studies. A single-crystal electrode, Cu(111), was used for EC-STM experiments.

Reagent grade chemicals and double-distilled water were used to prepare the following electrolytes:

0.1 M Na₂SO₄ at pH = 2.94, pH was adjusted using diluted sulfuric acid.

Investigated inhibitors

Thiazole derivatives:

- 5-benzylidene-2,4-dioxotetrahydro-1,3-thiazole (BDT)
- 5-(4'-isopropylbenzylidene)-2,4-dioxotetrahydro-1,3-thiazole (IPBDT)
- 5-(3'-thenylidene)-2,4-dioxotetrahydro-1,3-thiazole (TDT)
- 5-(3',4'-dimethoxybenzylidene)-2,4-dioxotetrahydro-1,3-thiazole (MBDT)

All experiments were done at open atmosphere and room temperature. Due to the low solubility of the tested thiazole derivatives, inhibitors were first dissolved into 20 ml of ethanol.

Electrochemical measurements

A three-electrode cell was used for the electrochemical impedance measurements (EIS), copper-working electrode, SCE- reference electrode, and Pt- counter electrode. The working electrode was constructed from high-purity copper rods (99.99% Cu). The electrode was wet-polished with SiC papers (grit sizes of 800 and 1200), rinsed with acetone and double distilled water, then immersed in the electrolyte solution. Measurements were performed at room temperature according to the procedure described in ASTM G-5-93 standard. A computer-controlled potentiostat (Model Solartron ECI-1286) and a frequency response analyzer (Solartron FRA-1250) were applied for the electrochemical measurements.

QCM measurements

The quartz crystal applied for this investigation had gold layers deposited at both sides (thickness 150 nm) over a thin layer of Cr (thickness 15 nm, for adhesion purpose). Copper layers were galvanostatically electrodeposited on one face of the crystal, facing the solution, at room temperature. The deposition bath contained 0.5 M CuSO_4 , 0.5 M H_2SO_4 , and 1 M $\text{C}_2\text{H}_5\text{OH}$ in double-distilled water. The cell reference and counter electrodes were SCE and a Pt wire, respectively.

The freshly deposited copper layer was investigated in three time intervals. In the first interval, the deposited Cu surface was exposed to the corrosive solution (0.1 M Na_2SO_4). Then, in the second interval, the solution was changed to an inhibitor-containing electrolyte for a longer exposure period. Finally, the solution was changed back to the corrosive electrolyte and the measurement was conducted until most of the deposited Cu was removed or there was no significant change of the electrode frequency. During all three intervals, frequency (mass) change was monitored. Data collected were analyzed and stored using specially developed software.

SPM measurements

In situ EC-STM measurements were performed using molecular imaging picostat. The tunneling tips were made of Pt and covered with an epoxy layer up to the operational tip, to decrease the Faradic current [20]. A three-electrode electrochemical cell was used, Cu(111)- working electrode and Pt wires-reference and counter electrodes.

The electrochemical potentials of the electrode and tip were independently controlled by means of a potentiostat. The working electrode was Cu(111) single-crystal. The sample was electrochemically polished in 66% ortho-phosphoric acid at an anodic potential 1.8 V vs. Cu counter electrode. Subsequently, it was rinsed with ultra-pure water and the clean sample was mounted in the STM cell, covered with the desired electrolyte.

RESULTS AND DISCUSSION

Electrochemical measurements

The electrochemical behavior of copper in acidic solution with the addition of thiazole derivatives was published in previous publication [16,17]. Figure 1 shows a typical electrochemical impedance spectroscopy (Nyquist and Bode) plots of copper electrode in 0.1 M Na_2SO_4 electrolytes without and with the addition of tested inhibitors. Polarization resistance values of the thiazole derivatives, in comparison to the blank aggressive solution, are depicted in Fig. 1a. R_p values were obtained by calculating the semicircle intersection with the real part of the impedance amplitude. It is clear that IPBDT pro-

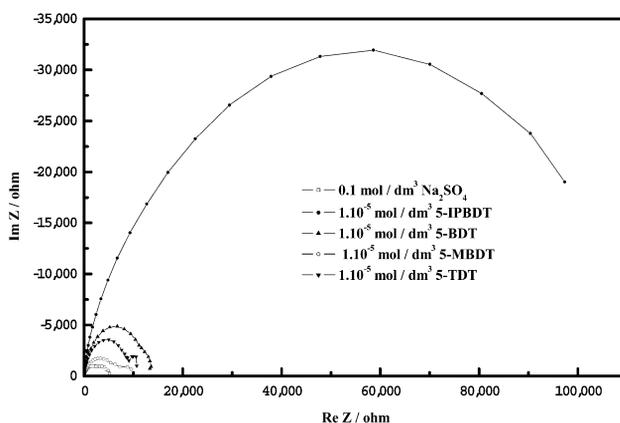


Fig. 1a Nyquist plot of EIS for the tested thiazole derivatives.

duced the highest R_p value, which is an indication of the formation of an effective protective film that hindered corrosion. The inhibition efficiency ($\eta\%$) was determined using the following formula:

$$\eta (\%) = (1 - R_p^{\text{inh}} / R_p^{\circ}) \cdot 100 \quad (1)$$

where R_p° and R_p^{inh} represent the electrode polarization resistance in the absence and presence of the inhibitor in the electrolyte, respectively.

Polarization resistances and inhibition efficiency results are presented in Table 1. The inhibitor 5-IPBDT produced the highest polarization resistance, thus the highest inhibition efficiency against Cu corrosion ($\eta = 93\%$). The order of protection produced by the EIS method is as follows: IPBDT > BDT > TDT > MBDT. This can be explained by the presence of N and S in the molecule structure, and the longer chain serves as a protecting shield on the copper electrode surface.

Table 1 EIS (R_p and η) results for the tested thiazole derivatives.

Inhibitor	IPBDT	BDT	TDT	MBDT
R_p (k ohm)	115	15	9.3	7.3
Inhibitor Efficiency %	93	86	80	71

Figure 1b shows the Bode plot for the tested thiazole derivatives. Phase shift vs. the log of the frequency gives an indication of the behavior of the protective film formed on the electrode surface due to the inhibitor adsorption. It can be seen from this figure that the process taking place at the electrode surface has one relaxation time constant. The location of the relaxation time constant did not change much from one inhibitor, but the phase shift value increased with IPBDT having the highest value at the peak location. This is an indication that the adsorption of all inhibitors on the electrode surface follows the same pattern but with different intensities [16]. In a further study, a model will be used to simulate the physical processes taking place at the electrode surface.

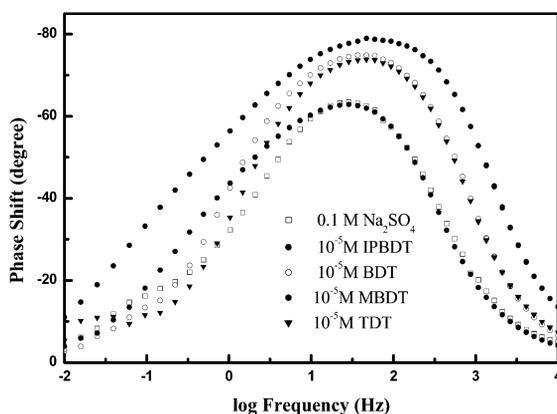


Fig. 1b Bode plot of EIS for the tested thiazole derivatives.

QCM results

QCM measurements were carried out in 0.1 M Na_2SO_4 solution without and with the addition of inhibitors. The adsorption properties of thiazole derivatives were studied, and the electrode mass change was monitored.

During the first interval, all experiments showed almost the same behavior. The electrode mass decreased, which means that the copper dissolution proceeds (Fig. 2). The similar behavior can be explained by the fact that conditions for this interval are the same for all experiments performed. Negligible deviations can be related to difference in surface roughness during Cu deposition. The addition of IPBDT and BDT show significant decreases in the electrode mass change during the second interval. These two thiazole derivatives slowed the Cu dissolution, and the electrode mass change almost stabilized in the case of IPBDT. TDT and MBDT did not produce as much protection as in the case of IPBDT and BDT. Absence of the inhibitor increased the corrosion rate, but not as high as in the

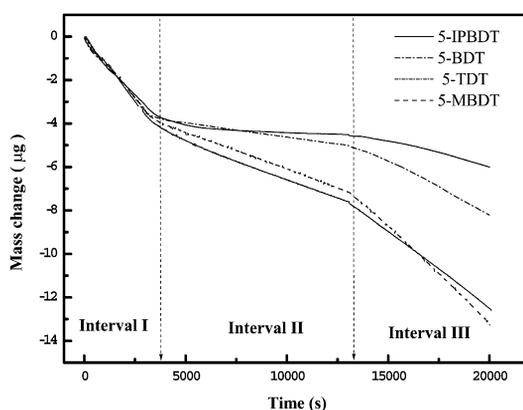


Fig. 2 Mass changes of Cu in acidic 0.1 M Na_2SO_4 solution without and with the addition of the tested thiazole derivatives in time.

first interval. This is due to the remaining adsorbed inhibitor molecules or complexes on the electrode surface. By using Faraday's law, the Cu thickness reduction rate was calculated as:

$$\delta = (\Delta m \cdot 3600 \cdot 24 \cdot 365 \cdot 10\,000) / A \cdot D \cdot t \quad (2)$$

where δ , thickness reduction rate [$\mu\text{m}/\text{yr}$]; Δm , mass loss; A , electrode surface area (cm^2); t , time (s); D , Cu density (g cm^{-3}).

The Cu electrode thickness reduction rate results, calculated using eq. 2, and the inhibition efficiencies of the tested thiazoles are tabulated in Table 2. The protection order result from QCM results was in good agreement with the electrochemical measurements.

Table 2 Thickness reduction rate of copper in 0.1 M Na_2SO_4 with and without the addition of thiazole derivatives

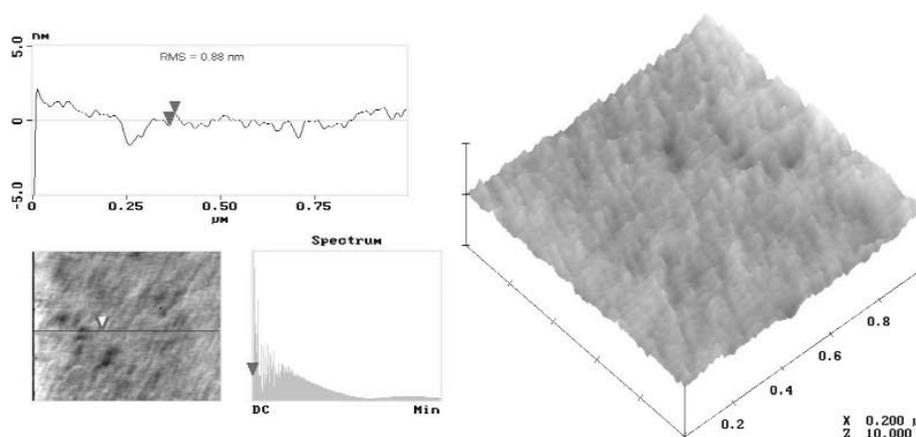
Solutions	Thickness reduction rate ($\mu\text{m}/\text{yr}$)	η (%)
Blank	126	-
IPBDT	15	89
BDT	18	86
TDT	44	65
MBDT	47	73

The QCM results showed that the adsorbed layers of the tested inhibitors are of a 2D type where a mono or even a sub-monolayer is adsorbed on the Cu surface. This result was also confirmed by other methods [16]. The EIS (R_p values) and the QCM analyses showed that the highest inhibitor efficiency is provided by IPBDT (more than 90%). These results are expected by molecular structure analysis, which predicted the effectiveness of those molecules due to their favorable structure.

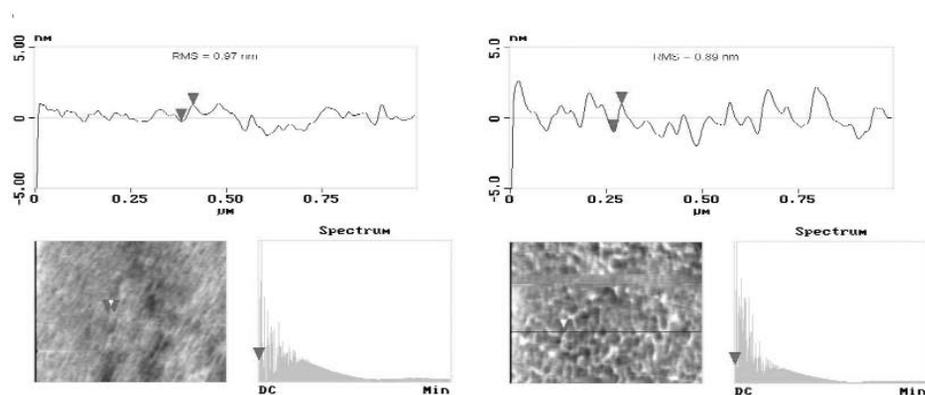
SPM results

The surface morphology was followed in presence of different thiazole derivatives using AFM. A Cu(111) single crystal was pretreated and electrochemically polished before each measurements. At an inhibitor concentration of 10^{-5} M, surface morphology without any structure changes could be observed at OCP, as seen in Fig. 3. Copper surface was covered with an inhibitor layer, which gets thicker in time, in the case of IPBDT. The surface roughness, which is represented by RMS values, varied with the addition of the inhibitors comparing to the electropolished surface. IPBDT produced the smoothest surface and thus was the most effective among the tested thiazole derivatives.

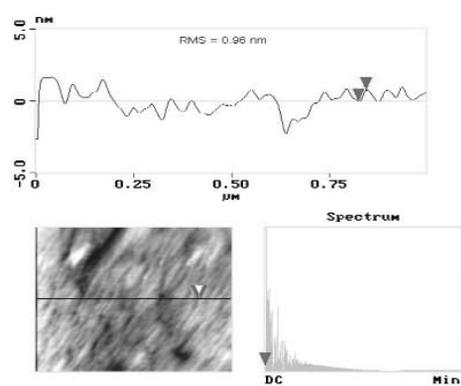
Figure 4 shows Cu(111) surface morphology developed shortly after changing the electrolyte to inhibitor-containing solution (10^{-5} M 5-IPBDT). The STM images give a clear indication of the reformation of the surface by the addition of the IPBDT. Presence of 5-IPBDT masked the atomic terraces and smoothed the surface, while the local imperfections are still visible. The atomic terraces (2.56 \AA) were still visible on some sites, which shows that the surface was partially covered with 5-IPBDT. The surface morphology did not change significantly during the measurement; only the stepped structure became less visible (Fig. 4). This result can be explained by the 5-IPBDT molecule reordering on the copper surface.



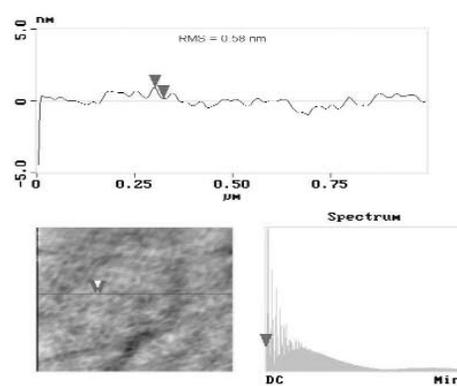
AFM results of an electropolished Cu surface



5-IPBDT



5-BDT



5-TDT

5-MBDT

Fig. 3 AFM images of Cu electrode surface without and with the addition of the tested thiazole derivatives.

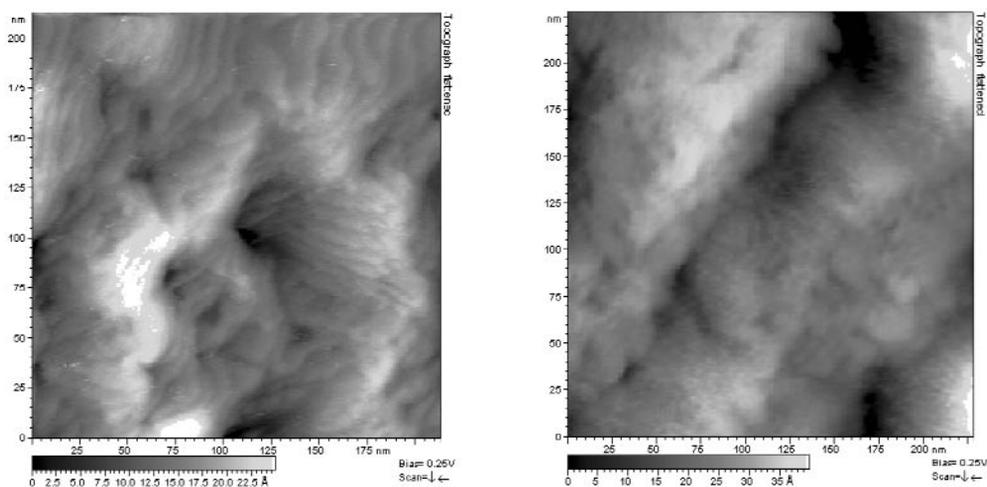


Fig. 4 STM images of Cu(111) surface in solution without and with the addition of IPBDT.

CONCLUSIONS

The inhibition effectiveness of thiazole derivatives (IPBDT, BDT, TDT, and MBDT) against copper surfaces was studied using EIS, QCM, and *in situ* SPM techniques. The results are summarized below:

- The presence of thiazole derivatives (especially IPBDT and BDT) hindered copper corrosion. The applied techniques showed that IPBDT, among the tested thiazole derivatives, produced the best protection against copper corrosion in acidic 0.1 M Na₂SO₄ solution.
- STM images in presence of IPBDT showed that the surface is partially covered with an inhibitor layer.
- The formed thiazole layers are very thin and might be in the monolayer order as shown by QCM and STM.
- The application of QCM technique provided real-time corrosion rate measurements as well as the monitoring of the inhibitor effectiveness. This thin layer hinders copper corrosion even in the absence of the inhibitor in the solution.
- The excellent protection provided by IPBDT is credited to its molecular structure. The longer chain improved the effectiveness and played an umbrella-type role.
- STM images in presence of IPBDT showed that the surface is covered with an inhibitor layer which thickness increased in time.
- The investigated thiazole derivatives (especially IPBDT) showed a great potential to replace toxic inhibitors (such as triazoles) that are applied in closed systems.

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