Original Article

The inhibition mechanism of a new synthesized indole derivative for copper in acidic environment via experimental and theoretical study

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The 3,3’-(4-(methylthio)phenyl)methylene)bis(1H-indole) (TPBI) of indole derivative was synthesized through the reaction of indole (ID) with 4-(methylthio)benzaldehyde. The electrochemical investigation showed that TPBI served as mixed-type inhibitor to protect copper against corrosion more efficiently than ID, which was further demonstrated by comprehensive characterizations. The efficient inhibitive performance was attributed to the self-assembled monolayers (SAMs) on the copper surface formed by the interaction of N and S atoms of TPBI with copper (I). Quantum calculations results further confirmed that the inhibitory effect of TPBI was better than ID.

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1. **Introduction**

Copper is one of the most widely applied metals in industry due to its high electrical and thermal conductivity [1–3]. However, impacted by the acid rain during the process of using, it was easy to form oxidized corrosion products on the surface of copper equipment, which caused a sharp drop in electrical conduction and heat transfer efficiencies of the equipment [4]. Therefore, pickling solutions, such as sulfuric acid, were often used to remove corrosion products from the surface of copper [5]. Unfortunately, sulfuric acid could also corrode copper. As a result, studies on the protection of copper against corrosion in acidic media have attracted much attention. One of the most effective strategies to prevent copper from corrosion in acidic environment was the use of organics as corrosion inhibitors [6–8]. Among these organic inhibitors, N and S atoms were often present, since they could easily chelate with copper surface to form self-assembled monolayers (SAMs), which were used as insulating layers to prevent the penetration of corrosive species [9–14]. In addition, the corrosion effect was improved when increasing the number of heterocyclic rings in organics. For instance, Gao and co-workers described that the increasing of number of N-heterocycles had a positive effect on anticorrosion performance of copper in seawater [2,15].

Indole is a class of readily available and less-toxic organic compound. In addition, the N-heterocycle in the indole skeleton could provide adsorption center to interact with copper surface. Carboxyl or chlorine substituted indoles have been disclosed as corrosion inhibitors [16,17]. However, the corrosion inhibition effect of indole with one N-heterocyclic ring
was far from satisfactory. Hence, we envisaged increasing the number of heterocyclic rings in indole derivative to improve the corrosion inhibition effect.

In this work, we firstly designed a new indole derivative (TPBI) bearing two N-heterocyclic rings. Then, the anticorrosion ability of TPBI and ID for copper in 0.5 M H₂SO₄ solution were studied by electrochemical experiments. The adsorption mechanism of TPBI was investigated by surface characterizations (FT-IR, XPS, SEM-EDS, and CA) and quantum calculations. These results revealed that increasing the number of heterocyclic rings in indole molecule had a significant effect on anticorrosion ability, and provided a new direction for designing new indole-based corrosion inhibitors.

2. Experiments

2.1. Synthesis and characterization of target molecule

TPBI was synthesized through a convenient and effective method as shown in Scheme 1. 4-(Methylthio)benzaldehyde (5 mmol), indole (10 mmol), ether (10 mL), BF₃·Et₂O (0.01 mmol) were added into a dry round bottom flask successively. The reaction mixture was stirred at room temperature for 2 h. After the reaction was completed, the reaction solvent was removed under vacuum and purified by silica gel column chromatography using ethyl acetate/petroleum ether (1/8, v/v) as the eluent to give the pure product as yellow solid in 85% yield. The synthesized TPBI was characterized by ¹H NMR and ¹³C NMR analysis in Figure S1 and S2.

2.2. Preparation of solution and self-assembled protective film

TPBI or ID was dissolved in ethanol to prepared different concentrations of solution. The copper specimens were meticulously ground with a variety of emery papers (400, 800, 1200, 2000 grits) to get a smooth surface, then washed with ultrapure water and ethanol continuously to remove all contaminants, finally, dried under a stream of nitrogen. After that, the prepared specimens were immersed in 10 mM inhibitor solutions for various time (1, 4, 8, 12 h) at 298 K. In addition, copper specimens were immersed in different concentrations of TPBI solution (1, 3, 6, 10 mM) for 12 h.

2.3. Electrochemical measurement

The electrochemical measurements were performed in three-electrode system. A modified copper sample acted as the working electrode, a saturated calomel electrode as the reference electrode, and a platinum plate as the counter electrode. Electrochemical impedance spectroscopy (EIS) was determined in the frequency range from 100 kHz to 0.01 Hz under the open-circuit potential (OCP) in a stable state. And the impedance parameters were fitted and analyzed by Zsimpwin software. The polarization curves were tested from −300 mV to +200 mV (versus OCP) at 1 mV s⁻¹ potential scanning rate. The corrosion inhibition efficiencies (η) were calculated from polarization curves and EIS according to the following equations [18,19]:

\[
\eta_P = \frac{j_{corr} - j_{corr, 0}}{j_{corr, 0}} \times 100
\]

\[
\eta_E = \frac{R_{ct} - R_{ct, 0}}{R_{ct}} \times 100
\]

Herein, \( j_{corr, 0} \) and \( j_{corr} \) were the corrosion current densities without and with the inhibitors, \( R_{ct, 0} \) and \( R_{ct} \) were the charge transfer resistances of copper electrodes without and with inhibitors, respectively.

2.4. Surface characterizations

Fourier transform infrared (FT-IR), energy-dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) were employed to investigate the adsorption mechanism of TPBI molecule self-assembled on copper surface. XPS measurement was carried on a PHI 5700 spectrometer with Al Kα anode (1486.6 eV). The surface wet ability was measured by contact angle (CA) under static. The surface morphology of the studied copper specimen was measured by scanning electron microscope (SEM) under high vacuum.

2.5. Theoretical calculation research

The software of the molecular dynamic simulation (Material Studio 7.0, Accelrys Inc.) was employed to research the quantum chemical calculations. The structures were optimized using the density functional theory (DFT).

3. Results and discussion

3.1. Optimum conditions for formation of the SAMs

3.1.1. Effect of self-assembly time

Polarization curves of the copper specimens measured in 0.5 M H₂SO₄ solution after immersion in 10 mM inhibitor solutions for various self-assembly time were revealed in Fig. 1. The polarization branches were extrapolated up to their point of intersection to acquire the corrosion current density (\( j_{corr} \)) and corrosion potential (\( E_{corr} \)) in Table S1 [20].

It was worth noting that the \( E_{corr} \) value of modified copper shifted toward to the negative direction slightly relative to the blank in Fig. 1. Meanwhile, the current density of modified copper decreased as compared with blank in the same condition. It was obvious that TPBI molecule (91.61%, 1 h) exhibited better corrosion inhibition efficiency than ID (54.75%, 1 h) under the same experimental condition as shown in Table S1. This indicated that the new TPBI inhibitor could form a more
compact protective film on copper surface than ID. In addition, the maximum negative shift values of $E_{\text{corr}}$ for TPBI and ID were 73 mV and 48 mV, respectively. The results indicated displacements were lower than 85 mV. Hence, TPBI and ID acted as mixed-type inhibitors [21].

The Nyquist plots of the copper specimens measured in 0.5 M H$_2$SO$_4$ solution after immersion in 10 mM inhibitor solutions for various self-assembly time were presented in Fig. 2. The symbols and the straight lines in all Nyquist plots were raw testing data and fitting data, respectively. Fig. 2(a) presented a depress semicircle in high frequencies with a straight line in low frequencies. And the straight line was attributed to Warburg impedance, which was caused by the transportation of dissolved oxygen and corrosion media to the copper surface [22]. In contrast, Fig. 2(b) showed a capacitive loop without a straight line, implying that TPBI inhibitor strongly prevented the diffusion process and the corrosion of copper was controlled by a charge transfer process. However, the capacitive loops were not perfect, probably because of the roughness and inhomogeneity of the copper electrodes [23]. Furthermore, the diameters of the curves were significantly increased along with the extending of self-assembly time.

The equivalent circuits were chosen to analyze the Nyquist plots in Fig. 3. The impedance of CPE was described as the followings [24,25]:

$$Z_{\text{CPE}} = \frac{1}{\omega^n Y}$$  \hspace{1cm} (3)

where $Y$ was the admittance of the electrochemical system, $j$ was the imaginary root, $\omega$ was for the angular frequency, and $n$ showed the deviation parameter. The value of $n$ typically ranged from $-1$ to 1. When $n = -1$, the CPE represented for an inductor, if $n = 0$, the CPE represented a pure resistor, if $n = 0.5$. 

Fig. 1 – Polarization curves of the copper specimens measured in 0.5 M H$_2$SO$_4$ solution after immersion in 10 mM ID (a) or TPBI (b) solutions for various self-assembly time.

Fig. 2 – Nyquist plots of the copper specimens measured in 0.5 M H$_2$SO$_4$ solution after immersion in 10 mM ID (a) or TPBI (b) solutions for various self-assembly time.

Fig. 3 – Equivalent circuit models fitting the EIS experimental data.
the CPE represented the Warburg impedance, and if \( n = 1 \), the CPE represented a pure capacitor [21].

Table S2 presented the impedance parameters derived from the equivalent circuits. The \( R_{ct} \) value of copper modified with TPBI (98.72%, 8 h) was distinctly higher than modified with ID (79.33%, 8 h), suggesting that TPBI was able to efficiently inhibit copper corrosion compared with ID. It was worth noting that when copper electrode was immersed in TPBI ethanol solution for 1 h and 12 h, the \( n_\% \) values were 92.96% and 99.10%, respectively. These results indicated that the process of forming TPBI-SAMs was a fast adsorption and then a slow rearrangement [8].

### 3.1.2. Effect of TPBI concentration

Electrochemical experiments were conducted to further explore whether the inhibition efficiency was affected by the concentration of TPBI solution. The results were shown in Tafel curves (a), Nyquist (b), Impedance (c), and Phase angle (d) images (Fig. 4). Clearly, the \( E_{corr} \) value of modified copper shifted toward to the negative direction slightly relative to blank in Fig. 4(a). And the polarization curves shifted to low current densities with increase of the concentrations of TPBI and reached the minimal value at 10 mM. However, the current density showed an increase at 12 mM relative to that at 10 mM. This phenomenon may be due to that the amounts of adsorbed inhibitor molecules reached a critical value and rearranged on the substrate [2], so that corrosive sulfate ions could easily attack copper electrode through the interspaces. Fig. 4(b) suggested that the diameter of capacitive loop increased with increasing the concentration of TPBI and reached maximum at 10 mM. The impedance plot (Fig. 4(c)) indicated that the copper specimens modified with TPBI showed high impedance values relative to blank. Additionally, it was found that the low-frequency impedance nearly increased two orders of magnitude compared with blank, suggesting that TPBI had good corrosion resistance. The phase angle plot in Fig. 4(d) showed the maximal phase angle became bigger with the increasing concentrations of TPBI and reached the maximal value at 10 mM. These results indicated that appropriate increased concentration of TPBI solution could form a more stable and dense protective film on copper electrode. Tables S3 and S4 showed polarization curves and impedance parameters of TPBI, respectively.

### 3.2. FT-IR analysis

The synthesized TPBI compound and the TPBI-SAMs on the copper substrate were studied by FT-IR and ATR-IR, respectively. The broad band at 3409.5 cm\(^{-1}\) was attributed to the v(N-H) [26], and the peak at around 3000 cm\(^{-1}\) was assigned to H\(_2\)O and vibration of C-H in phenyl ring [27] in Fig. 5. The stretching bands at 1456.4 cm\(^{-1}\) and 741.7 cm\(^{-1}\) corresponded to the C-N bond [28] and C-S bond [8,29], respectively. It was interesting that the peaks at 3409.5 cm\(^{-1}\), 1456.4 cm\(^{-1}\), and 741.7 cm\(^{-1}\) displayed a dramatical reduction, implying that TPBI molecule adsorbed on copper surface through chemical complexation of N and S atoms with copper ions.

### 3.3. XPS for TPBI-SAMs

XPS measurement was carried to explore the adsorption mechanism of TPBI molecule self-assembled on copper
surface. And the peaks of different elements on copper surfaces were detected after the copper specimens were covered without and with inhibitor immersed in 0.5 M H$_2$SO$_4$ solution for 12 h.

Fig. 6 presented the XPS survey spectra of the copper surfaces covered without and with TPBI immersed in 0.5 M H$_2$SO$_4$ solution for 12 h. The presence of C and O in the copper surface covered without inhibitor (referred to as Cu-bare in the followings) was attributed to carbon contamination. As compared with bare copper, some new peaks such as S2s, S2p, and N1s were presented in the XPS spectroscopy of copper surface covered with TPBI (referred to as Cu-TPBI in the followings). These results indicated that TPBI molecule adsorbed on the copper surface successfully.

### 3.3.1. XPS spectra of Cu 2p from the studied copper specimen surfaces

XPS spectra of Cu2p from the copper surfaces covered without and with TPBI immersed in 0.5 M H$_2$SO$_4$ solution for 12 h were presented in Fig. 7. The high-resolution spectra of Cu2p showed similar peak shapes and binding energies (Cu2p$_{3/2}$, 951.90 eV for bare copper, 952.35 eV for Cu-TPBI; Cu2p$_{3/2}$, 932.05 eV for bare copper, 932.50 eV for Cu-TPBI) that could be related to Cu (I) [15]. No satellite peaks were found between typical Cu2p$_{1/2}$ and Cu2p$_{3/2}$ in Cu2p spectra, which suggested that the inexistence of Cu (II) in the copper sample surfaces [2]. As discussed above the copper only transferred from Cu (0) to Cu (I) in the process of copper corrosion.

### 3.3.2. XPS spectra of C1s from the studied copper specimen surfaces

Fig. 8 showed de-convolution spectra of the C1s for the copper surfaces covered without and with TPBI immersed in 0.5 M H$_2$SO$_4$ solution for 12 h. The corresponding chemical states, full width at half maximum (FWHM), and binding energy were shown in Table S5. As shown in Fig. 8(a), C1s spectroscopy of surface from Cu-bare could be resolved into C–C, C–O, and O–C=O components which were located at 284.82, 286.20, and 288.35 eV as the result of adventitious carbon contamination [30,31]. The peak centered at 284.80 eV corresponded to the calibrated carbon, and C1s spectroscopy of surface from Cu-TPBI could be assigned to C–C=C=C (284.72 eV), C–S (285.53 eV), C–O (286.86 eV), and C–N/O=C=O (288.40 eV) as shown in Fig. 8(b) [32–35], indicating that the carbon contamination also existed in copper surface covered with TPBI. As compared with bare copper surface, C–S and C–N bonds were detected on copper surface covered with TPBI, demonstrating that the inhibitor adsorbed on copper surface successfully.

### 3.3.3. XPS spectra of N1s and S2p from the studied copper specimen surfaces

De-convolutions of N1s and S2p spectra for the investigated copper sample surface covered with TPBI immersed in 0.5 M H$_2$SO$_4$ solution for 12 h were showed in Fig. 9(a) and (b), respectively. The corresponding chemical states, FWHM, and binding energy were shown in Tables S6 and S7. The surveyed spectroscopy of N1s from Cu-TPBI presented mainly two peaks. The peak centered at 399.09 eV related to the bond of N–Cu produced by nitrogen atom with Cu (I) [36]. In addition, the peak at higher binding energy (400.38 eV) was corresponded to the bond of N–H in TPBI molecule structure [37]. Fig. 9(b) described the S2p spectroscopy of Cu-TPBI. It was obvious that two peaks at 163.20 eV and 164.39 eV were detected due to the existence of S–Cu bond [38,39]. Therefore, these results revealed that both N and S atoms combined with Cu (I) leading to the chemical adsorption, which was in keeping with FT-IR measurements.

### 3.4. Contact angle analysis of copper surfaces

The contact angle measurement was applied to explore the wet ability of the studied copper specimens. The contact angle values of the surfaces from polished copper and copper modified with TPBI were 70.5° and 100.6°, respectively (Fig. 10). It was known that hydrophobic structure was better able to
isolate air and prevent copper substrate from contacting corrosive media [40]. So, the copper surface modified with TPBI presented a good hydrophobicity. These results indicated that TPBI structure had a good hydrophobicity.

3.5. **SEM and EDS analysis of copper surfaces**

SEM and EDS measurements were employed to study the copper surfaces before or after immersion in 0.5 M H₂SO₄ solution for 12 h in Fig. 11. The polished copper presented a smooth and tidy metal surface (Fig. 11(a)), but the polished copper immersed in 0.5 M H₂SO₄ solution for 12 h exhibited a porous and rough surface due to the attack of sulfate ions (Fig. 11(b)). It was obvious that the protective layer of TPBI completely covered the copper surface in form of spherical adsorption layer (Fig. 11(c)). Meanwhile, the new peaks of N and S atoms were found in EDS image (Fig. 11(f)) as compared with the polished copper (Fig. 11(d)). These results demonstrated that TPBI adsorbed on the copper surface to form the protective layer, which was agreement with electrochemical experiments.
3.6. **Adsorption isotherm**

The adsorption mechanism of the inhibitor self-assembled on the copper surface was further studied by adsorption isotherm which was derived by fitting surface coverage ($\theta$) as a function of the TPBI concentration. Langmuir’s adsorption isotherm was obtained using the following formula [41]:

$$\frac{\theta}{1-\theta} = K \times C$$
wherein $K$ showed the equilibrium constant of the adsorption, and $c$ represented the concentration of the TPBI solution.

The $K$ was linked to the energy of adsorption ($\Delta G^\circ$) using the relation [42,43]:

$$K = \left( \frac{1}{55.5} \right) \exp \left( - \frac{\Delta G^\circ}{RT} \right)$$

(5)

where $R$ was the universal gas constant, and $T$ was the absolute temperature.

The plot of Langmuir isotherm yielded using linear regression of $c/\theta$ versus $c$ exhibited in Fig. 12. The linear regression coefficient was very close to 1 ($R^2 = 0.998$), which indicated that the adsorption of inhibitors at the copper-solution interface abided by Langmuir isotherm.

Thermodynamic parameters of the TPBI inhibitor were obtained from Langmuir adsorption isotherm in Table S8. A high value of $K$ and a low value of $\Delta G^\circ$ suggested that the TPBI inhibitor could firmly adsorbed on copper surface. The calculated value of $\Delta G^\circ$ was between $-40 \text{kJ/mol}$ and $-20 \text{kJ/mol}$, implying that the adsorption of TPBI on copper surface was attributed to both physisorption and chemisorption.

3.7. Theoretical calculation

The quantum calculation results of the two molecules were shown in Fig. 13. The HOMO and LUMO orbitals of ID were mainly concentrated on the entire molecular plane, indicating that the entire molecular plane was the reactive site of the molecule. TPBI had more active sites than ID, because it was distributed on the indole molecule, the benzene ring and the S atom. This also indicated that the TPBI easily and strongly adsorbed on the copper surface to form a passivation film. As seen in Table S9, TPBI showed a higher value of $E_{\text{HOMO}}$, which suggested it easily offered electrons [30]. In addition, the smaller energy difference ($\Delta E$) and the larger dipole moment ($\mu$) represented stronger reactivity [44], so the corrosion inhibition effect would be: TPBI > ID. Theoretical calculations provided a better basis for corrosion inhibition mechanisms and experimental conclusions.

4. Conclusion

In summary, a new indole derivative was synthesized through a concise method. The inhibition efficiency of TPBI was studied by electrochemical measurements, which indicated that TPBI as mixed-type inhibitor was able to efficiently inhibit copper corrosion compared with ID. FT-IR, EDS, XPS and CA measurements demonstrated that N and S atoms of TPBI interacted with copper surface to form a dense protective film. Additionally, the adsorption of TPBI on copper surface was attributed to both physisorption and chemisorption and abided by Langmuir isotherm. The theoretical calculations agreed with the experimental results. These systematic studies provided a new direction for designing new indole-based corrosion inhibitors.

![Fig. 12 – Langmuir adsorption isotherm of TPBI on copper surfaces in 0.5 M H$_2$SO$_4$ solution.](image)

![Fig. 13 – Molecular frontier orbital maps of ID and TPBI.](image)
Conflict of interest

We have no conflicts of interest to this work. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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Appendix A. Supplementary data


REFERENCES


