Pivotal Role of Heteroatoms in Improving the Corrosion Inhibition Ability of Thiourea Derivatives

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ABSTRACT: 1,3-Diphenyl-2-thiourea (DPTU) and 1-phenyl-3-(2-pyridyl)-2-thiourea (PPTU) were selected as the researched subject for investigating the effect of heteroatoms on the low carbon steel corrosion inhibition ability. Results from the potentiodynamic polarization measurements (PPM) indicate that the addition of a nitrogen atom in the benzene ring increases the corrosion inhibition efficiency of PPTU (97.2%), being higher than that of DPTU (93.1%) at the same condition of $2.0 \times 10^{-4}$ M at 30 °C. The Nyquist diagrams show that increasing the concentrations of both DPTU and PPTU will enhance the charge-transfer resistance and reduce the double-layer capacitance. The obtained data based on PPM and electrochemical impedance spectroscopy methods are in accordance to the analysis based on the scanning electrochemical microscopy images. Besides, results from quantum chemical calculations prove that the heteroatoms in the inhibitor molecules are the adsorption centers, and the benzene rings increase the electrostatic interaction between the inhibitor molecules and the steel surface. Results from Monte Carlo and molecular dynamics simulation have clarified the adsorption mechanism of DPTU and PPTU on the steel surface. Adsorption energies confirm that PPTU displays the higher inhibition ability as compared with DPTU.

1. INTRODUCTION

In the field of corrosion, the study of solutions to prevent metal corrosion is an important task that requires scientists to focus on research. There are many different methods to retard and prevent the metal corrosion such as designing materials to avoid corrosion, selecting suitable materials in each environment, protecting surfaces with coatings, electrochemical methods, and so forth. In particular, corrosion inhibitors are used as a low-cost way with high efficiency. Inhibitors perform their activities via the adsorption and the formation of a film on the metal surface. As a result, they reduce corrosion by increasing the polarization of the anode or cathode, limiting the movement or diffusion of ions onto the metal surface, and increasing the resistance of the metal surface.

Inorganic compounds containing sulfur or nitrogen atoms are evaluated as effective corrosion inhibitors for steel in acid solutions. In addition, the appearance of benzene rings in the inhibitor molecule is also an important factor because it increases the electrostatic interaction between the inhibitor and metal surface. As a result, it enhances the ability of metal inhibition in a long time. Therefore, when searching the potential corrosion inhibitors, organic compounds containing both heteroatoms and benzene rings are the promising options that should be considered.

Until now, there have been many studies on the ability to inhibit the corrosion of thiourea derivatives. In 2005, Jeyaprabha et al. selected poly(diphenylamine) as a studied corrosion inhibitor for iron in 0.5 M H$_2$SO$_4$ and compared it with diphenylamine monomer. They reported that poly(diphenylamine) performed as an efficient inhibitor with the maximum efficiency of 96% at very low concentration of 10 ppm where the monomer gave an efficiency of 75% at 1000 ppm. In 2006, cold-rolled steel corrosion inhibition ability of N-naphthyl-N’-phenylthiourea and N,N’-diphenylthiourea in 0.5 M H$_2$SO$_4$ were examined and reported by Harek and co-workers. The studied results revealed that substitution of phenyl by the naphthyl group increased the inhibition efficiency from 80.0 to 96.0% at the inhibitor concentration of 2.0 $\times$ 10$^{-4}$ M. In 2018, Zhang and co-workers investigated the inhibition ability of 1-(2-pyridyl)-2-thiourea and 2-(imidazole-2-yl)-pyridine. These compounds were determined as mixed-type inhibitors with the maximum inhibition efficiencies at 4.0 $\times$ 10$^{-4}$ M of 93.6% and 96.7%, respectively. In 2019, we chose 1-phenyl-2-thiourea (PTU) and 1,3-diisopropyl-2-thiourea (ITU) to investigate the effect of temperature and structure on their
inhibition ability in 1.0 M HCl solution. It was worth that their corrosion inhibition efficiencies increased as the temperature was up in the range of 30–60 °C. The theoretical results showed that PTU has more efficient inhibition ability than ITU because of the presence of benzene rings in its molecule. Obviously, these studies showed that thiourea derivatives have received the significant attention from researchers. However, the effect of heteroatoms on the corrosion inhibition performance has not been widely available and studied. In addition, the simple theoretical calculations did not show the adsorption configuration of the inhibitor molecules on the metal surface.

Because of the presence of N, S heteroatoms and benzene rings in the molecule of 1-phenyl-3-[(2-pyridyl)-2-thiourea (PPTU), it may transfer its electrons into empty d-orbitals of metal, to form strong metal-protective covering through coordinate bonding. Therefore, PPTU promises to become a potential corrosion inhibitor in acidic solution. For a comparison reason, 1,3-diphenyl-2-thiourea (DPTU) with less N atoms is also taken into account to evaluate the effect of heteroatoms on steel corrosion inhibition. In this research, we want to emphasize the role of heteroatoms on steel corrosion inhibition ability. In addition, the effect of temperature on corrosion inhibition processes was also studied. Theoretical calculations were used to explain the experimental results in detail. To attain this aim, quantum chemical calculations, Monte Carlo simulation, and molecular dynamics simulation were employed for establishing the correlation between molecular structure and corrosion inhibition performance.

2. RESULTS AND DISCUSSION

2.1. Effect of Concentration on Inhibition Efficiencies of DPTU and PPTU

2.1.1. Potentiodynamic Polarization Measurement. As shown in Figure 1, the polarization curves of steel are considerably changed with the presence of DPTU and PPTU. The corrosion current density changes from high to low magnitude with the increase of the inhibitor concentration. Figure 1a,b shows that the anode lines appear to overlap at all concentrations of DPTU, while these lines are more variable for PPTU. Besides, the cathode lines for both DPTU and PPTU are nearly parallel. This proves that the addition of inhibitors does not change the corrosion mechanism of the studied solution. The corrosion potentials shift toward negative potentials compared with the blank (1.0 M HCl). It may be inferred that DPTU and PPTU retard the hydrogen evolution reaction on the cathodic sites. As a result, the steel is protected from corrosive agents in solution.

At 30 °C, the inhibition efficiencies of DPTU are 93.1% at 2.0 × 10^{-4} M, 91.5% at 10^{-4} M, 89.9% at 5.0 × 10^{-5} M, and 84.9% at 10^{-5} M. However, the inhibition efficiencies of PPTU are 97.2% at 2.0 × 10^{-4} M, 96.6% at 10^{-4} M, 94.1% at 5.0 × 10^{-5} M and 92.6% at 10^{-5} M (Table 1). Clearly, in the 1.0 M HCl, PPTU always has higher steel inhibition performance than DPTU at the same conditions. The role of inhibitors displaces water molecules on the metal surface, blocks the active sites through adsorption, and forms a barrier film to prevent the corrosion process. Appearance of many heteroatoms in the PPTU molecule helps this molecule to closely link to the metal and increases its effective protection against the steel surface.

2.1.2. Electrochemical Impedance Spectroscopy. Electrochemical impedance spectroscopy (EIS) is used to provide an insight into the characteristics of electrochemical processes occurring on the steel surface in acid solution. Figure 2 shows Nyquist plots of low carbon steel in the absence and presence of inhibitors in 1.0 M HCl. They are semicircles shifted along the real impedance of the x-axis. However, the smoothness of these semicircles lightly deviated from the standard EIS theory.

![Figure 1a](https://dx.doi.org/10.1021/acsomega.0c04241)

**Table 1. Corrosion Parameters of Steel in 1.0 M HCl with Different Concentrations of Inhibitors at Different Temperatures**

| temperature (°C) | concentration (M) | DPTU H (%) | PPTU H (%) |
|------------------|-------------------|------------|------------|
| 30               | 2.0 × 10^{-4}     | 0.90       | 0.90       |
|                  | 1.0 × 10^{-4}     | 0.06       | 0.06       |
|                  | 5.0 × 10^{-5}     | 0.09       | 0.09       |
|                  | 1.0 × 10^{-5}     | 0.14       | 0.14       |
| 40               | 2.0 × 10^{-4}     | 1.01       | 1.01       |
|                  | 1.0 × 10^{-4}     | 0.16       | 0.16       |
|                  | 5.0 × 10^{-5}     | 0.21       | 0.21       |
|                  | 1.0 × 10^{-5}     | 0.24       | 0.24       |
| 50               | 2.0 × 10^{-4}     | 4.10       | 4.10       |
|                  | 1.0 × 10^{-4}     | 1.40       | 1.40       |
|                  | 5.0 × 10^{-5}     | 1.54       | 1.54       |
|                  | 1.0 × 10^{-5}     | 1.60       | 1.60       |
|                  | 7.35               | 1.90       | 1.90       |
|                  | 2.0 × 10^{-4}     | 3.75       | 3.75       |
|                  | 1.0 × 10^{-4}     | 3.98       | 3.98       |
|                  | 5.0 × 10^{-5}     | 4.25       | 4.25       |
|                  | 1.0 × 10^{-5}     | 4.44       | 4.44       |
|                  | 5.03               | 5.03       | 5.03       |

Figure 1. Potentiodynamic polarization curves of steel in 1 M HCl with different concentrations of (a) DPTU and (b) PPTU at 30 °C.
Imperfect capacitance loops may be caused by the heterogeneity of the metal surface and dispersion in frequency. As can be seen, the semicircle radii depend on the inhibitor concentration. The more the concentration increases, the radius of the semicircular lines increases. The diameters of the capacitance loops in the presence of DPTU and PPTU are bigger than those of the blanks, which suggests that inhibitor molecules can greatly promote anticorrosion of steel surface.

The results obtained in Nyquist plots can be interpreted in terms of equivalent circuit, as shown in Figure 3. This circuit includes the solution resistance \( R_s \) in parallel to the constant phase element (CPE) connected with the polarization resistance \( R_{dl} \). The impedance of the CPE can be given by equation

\[
Z_{CPE} = Y_0^{-1} (j \omega)^{-n}
\]

where \( Y_0 \) is the CPE constant, \( j \) is the imaginary number, \( \omega \) is the angular frequency \( (\omega = 2\pi f, f \) is the frequency), and \( n \) is the CPE exponent. The constant \( n \) serves to measure the surface heterogeneity. The double-layer capacitance \( (C_{dl}) \) can be simulated via CPE from the equation

\[
C_{dl} = Y_0 (\omega_{max})^{n-1}
\]

where \( \omega_{max} \) is the frequency corresponding to the maximum value of the imaginary component of the Nyquist plot.

The results in Table 2 show that \( R_s \) values increase with the increase of inhibitor concentration. While the \( R_s \) value of DPTU changes from 791 to 1778 \( \Omega \) cm\(^2\), this value of PPTU increases from 1678 to 3297 \( \Omega \) cm\(^2\). These may suggest that the inhibitors form a protective layer on the electrode surface at all of concentrations. This layer forms a barrier for mass and charge transfer. Thus, it can effectively prevent corrosive ions from directly contacting the working electrode. The higher \( R_s \) values of PPTU compared to those of DPTU indicate that PPTU can protect steel better than DPTU. Simultaneously, the addition of inhibitors decreases \( C_{dl} \) values, which is caused by forming a protective layer on the steel surface. The best inhibition efficiencies of PPTU and DPTU are 96.2 and 93.0% at the concentration of 2 \( \times \) 10\(^{-4} \) M according to the EIS method. It is clear that the results calculated from EIS are in line with the results from the potentiodynamic polarization measurement (PPM) method.

The different \( n \) values in the presence of inhibitors show that the heterogeneous properties of the steel surface are changed. This may occur because of the adsorption of inhibitor molecules on the electrode surface.

2.2. Effect of Temperature on Inhibition Efficiencies of DPTU and PPTU. Figure 4 shows that when the temperature increases, the inhibition performances of both DPTU and PPTU decrease. Specifically, the inhibition performance of DPTU decreases from 93.1 to 45.8% and that of DPTU decreases from 97.2 to 56.3% when the temperature changes in the range of 30–60 °C at the concentration of 2 \( \times \) 10\(^{-4} \) M. This hypotheses that as the temperature increases, DPTU and PPTU are separated from the steel surface, the metal is no longer protected, and so their corrosion inhibition performances reduce.

2.3. Adsorption Isotherms. To study the activity of inhibitor molecules on the metal surface, scientists have come up with various models of adsorption isotherms such as Temkin, Freundlich Langmuir, Brunauer—Emmett—Teller, Frumkin, Radke—Prausnitz, and so forth. In this study, the Freundlich model and Langmuir models are applied to study the adsorption of DPTU and PPTU on steel surface in 1.0 M HCl solution. The Freundlich model is expressed in the equation

\[
\theta = K_{ads} C^{1/n}
\]

The equation is rewritten as follows

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

The Langmuir equation is expressed in the following form

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

where \( K_{ads} \) is the equilibrium constant of the adsorption reaction and \( \theta \) is the surface coverage. The value of \( n \) is used to describe the ease of adsorption. When 0 < \( n < 1 \), adsorption is believed to be easy and moderate or difficult when \( n = 1 \) or \( n > 1 \), respectively.

Correlation coefficient \( (R^2) \) is used to evaluate the linearity of quantities in the Freundlich and Langmuir isothermal adsorption equations. \( R^2 \) of graph has a value of unit that
indicates that the adsorption of the molecule adheres to this model. Observing the data in Figure 5a,b, $R^2$ of the DPTU line at 40 °C and that of the PPTU lines at 30 and 60 °C are much different from the unit. These prove that the adsorption of DPTU and PPTU do not follow the Freudlich adsorption isotherm model.

The Langmuir adsorption isotherm model continues to be evaluated in Figure 6a,b. The values of $R^2$ are close to 1 for all graphs of DPTU and PPTU at the temperatures. However, the slopes of all graphs are different from unit. These prove that the adsorption of DPTU and PPTU does not obey the Langmuir isotherm and follows the modified Langmuir isotherm with the equation shown as follows23,24

$$\theta = \frac{C}{K_m C_{ads}} \quad (6)$$

The factor “m” is used to predict the number of molecules of the inhibitor absorbed per active site of low carbon steel.

2.4. Adsorption Thermodynamic Parameters. From the slopes of Langmuir equations, the values of $K_{ads}$ of DPTU and PPTU are calculated at the temperatures (Table 3). The relationship between adsorption constant ($K_{ads}$) and adsorption free energy ($\Delta G_{ads}$) is expressed by eq 23,26

$$\Delta G_{ads} = -RT \ln(55.5K_{ads}) \quad (7)$$

in which $T$ is the temperature of the study system (K), $R$ is the gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and the value of 55.5 is the concentration of water in the solution (M). The calculated values of $\Delta G_{ads}$ are shown in Table 3.

The standard adsorption enthalpy ($\Delta H_{ads}^0$) is calculated using Van’t Hoff equation

$$\frac{d \ln K_{ads}}{dT} = \frac{\Delta H_{ads}^0}{RT} \quad (8)$$

The equation can be changed27

$$\ln K_{ads} = \frac{-\Delta H_{ads}^0}{RT} + A \quad (9)$$

$A$: integral constant.

The values of $\Delta H_{ads}^0$ are drawn from the slopes of the lines, which show the relationship between $1/T$ and ln $K_{ads}$ (Figure 7). Standard adsorption entropy ($\Delta S_{ads}^0$) is calculated using thermodynamic eq 1028

$$\Delta S_{ads}^0 = \frac{\Delta H_{ads}^0 - \Delta G_{ads}^0}{T} \quad (10)$$

Observing Table 3, the negative values of $\Delta H_{ads}^0$ show that the adsorption process of DPTU and PPTU on the steel surface is an
exothermic process. If the value of $\Delta G_{ads}^0$ is within $-20 \text{ kJ mol}^{-1}$ or less negative, then the adsorption process is physical, and if the value of $\Delta G_{ads}^0$ is within $-40 \text{ kJ mol}^{-1}$ or more negative, the adsorption process is chemical.29 The $\Delta G_{ads}^0$ values of DPTU and PPTU indicate that they are involved in the chemical adsorption on the steel surface. The inhibitor molecules share or transfer electrons to the metal surface to form a co-ordinate type of bond.30

Positive values of $\Delta S_{ads}^0$ show an increase of the disorder on the steel surface in HCl solution. It is due to the adsorption of DPTU and PPTU molecules and desorption of water molecules on the steel surface.

2.5. SEM Analysis. Figure 8a,b shows the images of the steel surface before and after corrosion of acid solution. There are serious corrosion cracks and holes on the surface of carbon steel (as shown in Figure 8b). The metal surface is completely corroded and covered with flake-like corrosion products. However, in the presence of DPTU and PPTU, the carbon steel surface is relatively well preserved. The phenomenon of pits and holes (Figure 8b) has been reduced. The surface of steel in the presence of PPTU looks more smooth than that of DPTU. This is consistent with the high inhibition performance of PPTU and DPTU obtained by the electrochemical methods.

2.6. Quantum Chemical Calculations. The adsorption centers of inhibitors are determined through Mulliken charges.31 The more negatively charged the atoms are, the easier they are to donate the electrons. The data in Table 4 show that N and S atoms are electron-donating positions for DPTU and PPTU. Optimized structures, highest occupied molecular orbital (HOMO), and lowest unoccupied molecular orbital (LUMO) of DPTU and PPTU at B3LYP/6-311G(d,p) are shown in Figure 9. The HOMO and LUMO can display the electron-donating and -accepting positions of the molecule.32 Based on HOMO in Figure 9, DPTU and PPTU have a tendency to give electrons to the metal surface at S, N atoms. In contrast, the shapes of LUMO indicate that all positions in these molecules may receive electrons from iron metal.

Quantum chemical parameters such as HOMO energy ($E_{HOMO}$), LUMO energy ($E_{LUMO}$), energy gap ($\Delta E_{L-H}$), absolute electronegativity ($\chi$), absolute hardness ($\eta$), and global softness ($S$) are calculated for both DPTU and PPTU (Table 5). In the case of the neutral form, the obtained results from Table 5 show that the most quantum chemical parameters of both DPTU and PPTU have the same values. It indicates that the interaction of neutral studied compounds with the metal surface is similar.

The corrosion inhibition of DPTU and PPTU is investigated in acid solution, so these compounds can undergo protonation at the positions of the heteroatoms (N, S). Determination of the

### Table 3. $K_{ads}$, $\Delta G_{ads}^0$, $\Delta H_{ads}^0$, and $\Delta S_{ads}^0$ Values of DPTU and PPTU Adsorption Processes

| inhibitors | temperature (°C) | $K_{ads}$ (M$^{-1}$) | $\Delta G_{ads}^0$ (kJ mol$^{-1}$) | $\Delta H_{ads}^0$ (kJ mol$^{-1}$) | $\Delta S_{ads}^0$ (J mol$^{-1}$ K$^{-1}$) |
|------------|------------------|----------------------|----------------------------------|----------------------------------|----------------------------------|
| DPTU       | 30               | 589,908              | -44                              | -42                              | 5                                |
|            | 40               | 333,300              | -44                              | -42                              | 4                                |
|            | 50               | 237,834              | -44                              | -42                              | 6                                |
|            | 60               | 123,031              | -44                              | -42                              | 4                                |
| PPTU       | 30               | 886,270              | -45                              | -27                              | 58                               |
|            | 40               | 740,736              | -46                              | -27                              | 60                               |
|            | 50               | 604,320              | -47                              | -27                              | 61                               |
|            | 60               | 321,895              | -46                              | -27                              | 58                               |
stable forms of these protonated inhibitor molecules is necessary. Protonated sites are at S1, N2, and N3 for DPTU; S1, N2, N3, and N4 for PPTU. Seven protonated configurations of DPTU and PPTU optimized at the theoretical level of B3LYP/6-311G(d,p) and their relative energy (in parentheses) are shown in Figure 10. pDPTU-S1 and pPPTU-N4 have the

Table 4. Mulliken Charges of DPTU and PPTU

|       | DPTU |     |     |     |     |     |     |     |
|-------|------|-----|-----|-----|-----|-----|-----|-----|
| atoms | S1   | N2  | N3  | C4  | C5  | C6  | C7  | C8  |
| charges | −0.3 | −0.4| −0.5| 0.1 | 0.2 | 0.2 | −0.1| −0.1|
| atoms  | C9   | C10 | C11 | C12 | C13 | C14 | C15 | C16 |
| charges | −0.1 | −0.1| −0.1| −0.1| −0.1| −0.1| −0.1| −0.1|
| atoms  | S1   | N2  | N3  | N4  | C5  | C6  | C7  | C8  |
| charges | −0.2 | −0.2| −0.2| −0.3| 0.1 | 0.0 | 0.0 | 0.3 |
| atoms  | C9   | C10 | C11 | C12 | C13 | C14 | C15 | C16 |
| charges | 0.2  | 0.0 | 0.0 | 0.0 | −0.1| 0.1 | −0.1| 0.2 |

Figure 8. Scanning electrochemical microscopy (SEM) images of the low-carbon steel surface (a) before corrosion, (b) in 1.0 M HCl, (c) in 2 × 10⁻⁴ M DPTU, (d) in 2 × 10⁻⁴ M PPTU.

Figure 9. Optimized structures, HOMO, and LUMO of DPTU and PPTU.
lowest energy in these configurations, so they are selected for further studies.

The quantum chemical parameters of protonated inhibitors are calculated in Table 5. $E_{\text{LUMO}}$ of pPPTU-N4 (−6.1 eV) is lower than $E_{\text{LUMO}}$ of pDPTU-S1 (−4.9 eV), while $E_{\text{HOMO}}$ of pPPTU-N4 (−10.1 eV) is similar to that of pDPTU-S1 (−10.5 eV). Therefore, the ability of accepting electrons of pPPTU-N4 is greater than that of pDPTU-S1. The energy gap ($\Delta E_{\text{LUMO}-\text{HOMO}}$) is an important descriptor, which indicates the reactivity (adsorption) of inhibitors toward the metal surface. The organic compound with a low value of energy gap is generally characterized by good inhibition efficiency. The $\Delta E_{\text{LUMO}-\text{HOMO}}$ value of pPPTU-N4 is lower than that of pDPTU-S1. In addition, the values of $\eta$, $S$, and $\Delta N$ in Table 5 indicate that pPPTU-N4 can protect the steel surface better than pDPTU-S1. That is in good agreement with the experimental result of inhibition efficiencies.

2.7. Monte Carlo Simulation and Molecular Dynamics Simulation. The electrostatic energy, van der Waals energy, average total energy, intramolecular energy, and total energy for the inhibitor on the Fe(110) surface are calculated by optimizing the whole system and presented in Figure 11.

The most stable adsorption configurations are shown in Figure 12; it can be noticed that two inhibitors adsorb nearly parallel (side view) to the iron surface through the donation of $\pi$ electrons of the benzene rings and the lone pair of the heteroatoms to the metal.

The distance between atoms in the inhibitor molecule and the metal surface can help us to understand the nature of the adsorption process. When this distance is less than 3.5 Å, it is chemical adsorption. In contrast, this length value is greater than 3.5 Å, and van der Waals force is considered as the main interaction of the adsorption. The shortest distances between C, N, and S atoms of DPTU molecules and the surface of Fe(110) are of 2.9 Å; 2.9 Å; and 4.2 Å, respectively. In addition, the corresponding distances with regard to the PPTU molecule are 2.4, 2.3, and 2.7 Å. Based on these calculated values, it can be concluded that chemical adsorption takes place when DPTU and PPTU molecules contact with the iron surface.

Table 5. Quantum Chemical Parameters of DPTU and PPTU in the Gas Phase and in Acid Solution at B3LYP/6-311G(d,p)

| inhibitors | $E_{\text{HOMO}}$ (eV) | $E_{\text{LUMO}}$ (eV) | $\Delta E_{\text{LUMO}-\text{HOMO}}$ (eV) | $\chi$ (eV) | $\eta$ (eV) | $S$ (eV$^{-1}$) | $\Delta N$ |
|------------|----------------------|----------------------|---------------------------------|----------|----------|----------------|--------|
| DPTU       | −5.8                 | −1.4                 | 4.5                             | 3.6      | 2.2      | 0.5             | 0.8    |
| PPTU       | −5.7                 | −1.3                 | 4.4                             | 3.5      | 2.2      | 0.5             | 0.8    |
| pDPTU-S1   | −10.5                | −4.9                 | 5.6                             | 7.7      | 2.8      | 0.4             | −0.1   |
| pPPTU-N4   | −10.1                | −6.1                 | 4.0                             | 8.1      | 2.0      | 0.5             | −0.3   |
active centers are N, S, and benzene rings for PPTU, N, and benzene rings for DPTU. Benzene rings play important roles in increasing the cover during metal surface protection. The N4–Fe bond distance has the shortest value in all the bonds of PPTU, which proves that PPTU binds to the strongest Fe surface at this position. Clearly, this heteroatom plays an important role in stabilizing the interaction between the molecule and the iron surface. It gives the lone pairs of electrons to the empty d orbital of iron and forms stable coordinate bonds with the iron surface. The distances between the atoms of the PPTU molecule are smaller than those of DPTU, which again confirm that the link between PPTU and iron surface is stronger than that of DPTU. This is the reason the metal corrosion inhibition efficiency of PPTU is always higher than that of DPTU at the same conditions.

The adsorption energy of PPTU in Table 6 has a value of $-535 \text{ kJ mol}^{-1}$. It is more negative than the value of DPTU ($-509 \text{ kJ mol}^{-1}$). It indicates that PPTU adsorbs on a metal surface more strongly than DPTU.

Molecular dynamics simulation is applied to study the interaction of protonated inhibitors on the Fe(110) surface in 1.0 M HCl solution at 303 K. Figure 13 shows the side view and top view of pDPTU-S1 and pPPTU-N4 adsorption. These pDPTU-S1 and pPPTU-N4 molecules approach closely to the iron surface and have a large surface area. This gives them the ability to cover and form Fe protective films from corrosive agents in the solution.

In molecular dynamics simulation, interaction energy and binding energy are the important parameters to evaluate the corrosion inhibition capacity of inhibitor molecules. The negative value of the interaction energy indicates the strong interaction between the inhibitor molecule and the metal surface, while the large value of the binding energy shows the strong and durable adsorption of the inhibitor molecule.
The results in Table 7 show that the binding energy and the interaction energy values of pPPTU-N4 and pDPTU-S1 are not significantly different. Thus, the molecular dynamics simulations in this case mainly show the interaction configurations of protonated inhibitor molecules in acidic solution. They cannot compare the strength or weakness of the bonds.

### 2.8. Mechanism of Corrosion Inhibition

Hydrochloric acid solution contains H\(^+\) cations and Cl\(^-\) anions. In acidic media, DPTU and PPTU are protonated at the position of the heteroatoms, thus they are positively charged. Meanwhile, Cl\(^-\) ions are adsorbed on the positively charged metal surface through electrostatic interaction forming an iron-chloro complex. Next, protonated inhibitor molecules quickly move to the metal surface and adsorb onto it. 

\[
\begin{align*}
\text{Fe} + \text{H}_2\text{O} & \rightarrow \text{FeOH}_{\text{ads}} + \text{H}^+ + \text{e}^- \\
\text{FeOH}_{\text{ads}} + \text{Cl}_{\text{ads}} & \rightarrow \text{FeCl} + \text{OH}^- \\
\text{FeCl} & \rightarrow \text{Fe}^{2+} + \text{Cl}^- + \text{e}
\end{align*}
\]

(11)

The HOMO orbitals of these compounds are mainly located at thiourea groups, so these groups are the adsorption centers of iron. At this time, iron-inhibitor complexes are formed according to the following equation:

\[
\begin{align*}
\text{Fe}^{2+} + x\text{Cl}^- + y\text{H}_2\text{O} + z\text{DPTU} & \rightarrow [\text{Fe(DPTU)}_x(\text{OH})_y(\text{Cl})_z]^ {2-x-y} + y\text{H}^+ \\
\text{Fe}^{2+} + x\text{Cl}^- + y\text{H}_2\text{O} + z\text{PPTU} & \rightarrow [\text{Fe(PPTU)}_x(\text{OH})_y(\text{Cl})_z]^ {2-x-y} + y\text{H}^+
\end{align*}
\]

(12)

The formed complex adsorbs on the anodic sites and reduces the anodic dissolution of mild steel. On the other hand, cationic species can be adsorbed directly on cathodic sites and retard the rate of the hydrogen evolution reaction. As a result, the metal surface is protected. There are more heteroatoms in PPTU than in DPTU, which gives PPTU the capacity to bind the iron surface well. As a result, PPTU can protect the metals from corrosive agents better than DPTU.

### 3. CONCLUSIONS

Investigating low carbon steel corrosion inhibition of DPTU and PPTU with PPM, EIS, and SEM analysis as well as quantum chemical calculations, Monte Carlo simulation, molecular dynamics simulation, and some conclusions can be summarized as follows:

1. PPM gives the inhibition efficiencies of DPTU as 93.1% at \(5 \times 10^{-4}\) M, 91.5% at \(10^{-4}\) M, 89.9% at \(5 \times 10^{-3}\) M, and 84.9% at \(10^{-3}\) M, while the inhibition efficiencies of PPTU are 97.2% at \(2 \times 10^{-3}\) M, 96.6% at \(10^{-3}\) M, 94.1% at \(5 \times 10^{-3}\) M, and 92.6% at \(10^{-3}\) M at 30 \(^\circ\)C.

2. The trend of the inhibition efficiencies obtained from EIS is quite similar to the results from PPM. With increasing concentration of the inhibitor, the inhibition efficiencies reach a maximum value of 93.0% for DPTU and 96.2% for PPTU at \(2 \times 10^{-4}\) M.

3. The inhibition efficiencies of both DPTU and PPTU decrease when increasing the temperature. The adsorption of DPTU and PPTU both follow the modified Langmuir adsorption isotherm. The signs of \(\Delta G\) and \(\Delta H\) show that the adsorption processes are spontaneous and exothermic.

4. The SEM analysis shows that the metal surface is effectively protected in acid solution in the presence of inhibitors.

5. The presence of many heteroatoms in the PPTU molecule makes PPTU inhibit low carbon steel corrosion better than DPTU.

6. Quantum chemical calculations and Monte Carlo simulations are obtained in full accordance with experimental methods. Molecular dynamics simulation shows the interaction between protonated inhibitors with the Fe\((110)\) surface.

### 4. EXPERIMENTAL DETAILS AND COMPUTATIONAL METHODS

#### 4.1. Materials

The percentage weight composition of low carbon steel involves 98.2% Fe, 0.28% C, 0.4% Si, 1.1% Mn, 0.0% P, and 0.0% S. It is used as a working electrode with one surface area of 0.196 \(\text{cm}^2\), and the remaining areas are totally covered with layers of epoxy for isolation with the environment.

#### 4.2. Potentiodynamic Polarization Measurement

The metal corrosion inhibition ability of inhibitors was studied by the polarization curve method on the PGS-HH3 device of the Vietnam Academy of Science and Technology at temperatures ranging from 30 to 60 \(^\circ\)C with a step size of 10 \(^\circ\)C. Electrochemical measurements were performed on the CFAiochHISB-meter with a three-electrode system, in which the working electrode was low carbon steel, the comparison electrode was Ag/AgCl in saturated KCl, and the counter electrode was stainless steel with a large area.

Corrosion potential was scanned from \(-1.00\) to 0.20 \(V\) with a sensitivity of 7. Investigated concentrations of inhibitors were \(1.0 \times 10^{-5}\), \(5.0 \times 10^{-5}\), \(1.0 \times 10^{-4}\), and \(2.0 \times 10^{-4}\) M. Ethanol was added into the solution to ensure the solubility of inhibitors. The surface of the working electrode was abraded with metallographic emery paper and then was washed with distilled water, acetone, and finally was dried.

The corrosion inhibition efficiency (H %) was calculated by the following formula:

\[
H\% = \frac{i_{\text{corr}} - i_{\text{inh}}}{i_{\text{corr}}} \times 100
\]

(13)

where \(i_{\text{corr}}\) is the corrosion current density in the absence of inhibitors (\(\text{mA cm}^{-2}\)) and \(i_{\text{inh}}\) is the corrosion current density in the presence of inhibitors (\(\text{mA cm}^{-2}\)).

Surface coverage was calculated based on the following equation:

The presence of many heteroatoms in the PPTU molecule makes PPTU inhibit low carbon steel corrosion better than DPTU.

4. Quantum chemical calculations and Monte Carlo simulations are obtained in full accordance with experimental methods. Molecular dynamics simulation shows the interaction between protonated inhibitors with the Fe\((110)\) surface.
\[ \theta = \frac{i_{\text{corr}} - i_{\text{inh}}}{i_{\text{corr}}} \]  

(14)

4.3. Electrochemical Impedance Spectroscopy. At open-circuit potential, EIS was measured with an alternating current of 10 mV. A frequency range was used from 10 mHz to 100 Hz. The total number of points was 30. The EIS was recorded by a IM6 electrochemical meter from Zahner Elektrik of Germany, and Thales 4.5 software was used for simulation.

The corrosion inhibition efficiency was calculated according to eq 15[45,46]

\[ \text{H} \% = \frac{R_{\text{ct(inh)}} - R_{\text{ct}}}{R_{\text{ct}} \times 100} \]  

(15)

where \( R_{\text{ct}}(\Omega \text{ cm}^2) \) and \( R_{\text{ct(inh)}}(\Omega \text{ cm}^2) \) are charge-transfer resistances in the absence and presence of an inhibitor.

4.4. Scanning Electrochemical Microscopy. The low carbon steel samples were cleaned and immersed in 1.0 M HCl in the absence and presence of 2.0 × 10^{-4} M inhibitors for 24 h at room temperature. Then, the JSM-6010PLUS/LV scanning electron microscope was used to analyze the surface of steel with an energy-dispersive X-ray analyzer.

4.5. Quantum Chemical Calculations. All quantum chemical parameters were calculated based on the density functional theory integrated in the Gaussian 09 program. The geometry structures of compounds were first optimized at B3LYP/6-311G(d,p). Based on the output file, all quantum chemical parameters were calculated, including the HOMO and LUMO energy levels, Mulliken charge density, LUMO−HOMO energy gap (\( \Delta E_{\text{LUMO-HOMO}} \)), absolute electronegativity (\( \chi \)), chemical potential (\( \mu \)), absolute hardness (\( \eta \)), global softness (\( S \)), dipole moment, and number of transferred electron (\( \Delta N \)).

4.6. Monte Carlo Simulation and Molecular Dynamics Simulation. The interaction between the inhibitor molecule and the Fe(110) surface was studied and analyzed via Monte Carlo and molecular dynamics simulations. These simulations were carried out using Materials Studio 8.0 software. The geometry optimization of inhibitors was performed at DMol3 with the B3LYP functional, basis set of DNP, and basis file of 3.5. The Fe crystal was combined and cleaved along the plane (110). The simulations were carried out in a box of dimensions (41.15 × 36.58 × 29.97 Å3) with a time step of 0.1 fs and a simulation time of 500 ps. COMPASS force fields were used for simulations of all atoms and the structure of molecules. Monte Carlo simulation of the inhibitor on the Fe(110) surface was performed in the gas to determine its most stable interaction form based on the adsorption energy value. Besides, molecular dynamics simulation was used to predict and analyze the interaction between the inhibitor molecule and the Fe(110) surface in solution. In 1.0 M HCl, the ratio between H₂O and HCl was 500/9.[52] Based on this way, 491 molecules of H₂O, 9 Cl⁻, and 9 H₂O⁺ were added to the inhibition system in the simulation box. However, the inhibitor molecules were protonated in acidic solution, and the proportion of the constituents in the corrosive solution would consist of 492 H₂O, 9 Cl⁻, and 8 H₂O⁺ molecules and 1 protonated inhibitor. The interaction between the inhibitor and the Fe(110) surface could be assessed through binding energy (\( E_{\text{binding}} \)) and interaction energy (\( E_{\text{interaction}} \)), and these quantities can be calculated by the following equations:

\[ E_{\text{interaction}} = E_{\text{total}} - (E_{\text{surface+solution}} + E_{\text{inhibitor}}) \]  

(16)

in which \( E_{\text{total}} \) is the total energy of the entire system, \( E_{\text{surface+solution}} \) is the total energy of the Fe(110) surface and the solution in the absence of inhibitors, and \( E_{\text{inhibitor}} \) is the energy of the inhibitor.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04241.

Cartesian coordinates of DPTU, PPTU, pDPTU, and pPPTU in the gas phase optimized at B3LYP/6-311G(d,p) (PDF)

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Notes

The authors declare no competing financial interest.

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