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Experimental investigation for corrosion inhibition of mild steel in hydrochloric acid bath by 3-((5-phenyl-1,3,-thiadiazol-2-yl)imino)-2-oxoindoline

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Abstract

We examined the anti-corrosion activity of mild steel corrosion in hydrochloric acid (1 M) media caused by the Schiff base 3-((5-phenyl-1,3,4-thiadiazol-2-yl)imino)-2-oxoindoline (PTIO). Weight-loss measurements and scanning electron microscopy were performed during the investigation. The measurements showed that the inhibition efficiency of chemical compound increased with its increasing concentration. This inhibitor functioned through adsorption following the Langmuir isotherm and the electronic properties obtained through the Austin Model 1. Semi empirical method was found to be correlated with the inhibitor's experimental efficiency by the nonlinear regression method. The organic compound was synthesized effectively through a reaction between indoline-2,3-dione and 5-amino-2-phenyl-1,3,4-thiadiazol. Various spectroscopic techniques were used to characterize the synthesized inhibitor.

Keywords: Oxoindoline, weight-loss measurements, scanning electron microscopy, Austin Model 1.

Introduction

Alloys such as mild steel [1], ternary alloy [2], AlGaN [3] and Al3Ti0.5V0.5 alloy [4], are most important due to using it in a wide range of industrial applications. Corrosion is a destructive chemical phenomenon that attacks metals through reactions in the surrounding environment and causes constitutional damage. Hence, corrosion investigations are valuable. The investigation of anti-corrosion approaches by natural and synthetic molecules has been relatively efficient study domain [6]. According to researchers, corrosion inhibition fundamentally depends on the inhibitor's physiochemical and electronic properties, which are correlated with the inhibitor's structure (heteroatoms with steric effects) and electronic density [7]. inhibition mechanisms have been generally demonstrated through adsorbed process that done according to physical or chemical coated film approach on a mild steel surface [8]. Organic molecules that act as excellent inhibitors possess heteroatoms, S, N, P, and O [9–11]. To clarify the mode of action of organic molecules as inhibitors, we investigated the structural configuration and reactivity of adsorbed organic molecules (inhibitors) in their interaction with mild steel surface. Currently, theoretical calculations are utilized to elucidate the inhibitory mechanism. These calculations are beneficial in realizing the correlation between corrosion and the inhibitory properties of the utilized organic corrosion inhibitors [12]. Numerous articles reported on the theoretical investigation of the anticorrosive properties of organic molecules. These investigations mainly focused on quantum chemical calculations for organic compounds that may be used as inhibitors and on the correlation with the inhibitors' experimental efficiencies [13,14].

Researchers established the relation between the experimental and theoretical investigations of corrosion. The effectiveness of isomthane in inhibiting mild steel (MS) corrosion in acidic solutions was also confirmed [14–35]. In the present study, PTIO was synthesized, and its molecular structure was verified using CHN and spectroscopic methods. The effectiveness of the present organic inhibiting mild steel corrosion in HCl (.50 mM) was investigated by SEM and weight-loss techniques.

Experimental Section

All materials had been purchase through company named Sigma/Aldrich/ Malaysia and were tested by chromatography technique utilizing thin-layer method for purity investigation. The spectrum of infrared for PTIO was gained by a ThermoScientific NICOLET 6700 IR spectrometer. spectra for Nuclear magnetic resonance had been gained utilizing a JEOL JNM-ECP 400.

Synthesis of PTIO

A solution of indoline-2,3-dione ($5x10^{-3}$ mole) and 5-phenyl-1,3,4-thiadiazol-2-amine ($5x10^{-3}$ mole) in methyl alcohol (30 mL) have been well stirred and refluxed for 6 h with drops of glacial acetic acid. Subsequently. The filtration process was used for isolation of solid, washed repeatedly, and recrystallized from methanol. The obtained yield was 71%. The conditions for fluorescence transform infrared spectroscopy were 3392 (N–H str.), 3097 (Ar C–H str.), 1703 (–C=O str.), 1599 (C=N str.), 1415 (C–N str.), and 701 (C–S–C str.). The conditions for ^{1}H NMR (δ ppm, DMSO-d6) were 8.31 (s, 1H, –NH) and 7.01–8.02 (m, Ar–H).

Weight-loss Method

Mild steel coupons were obtained from Metal Company Samples and applied as electrode. The weight compositions of the mild steel coupons were as follows: [99.21 Fe], [0.21 C], [0.38 Si], [0.09 P], [0.05 Mn], and [0.05 Al]. On the basis of the standard investigation (G1-03) published in ASTM, the MS surface was cleaned. The coupons were immersed in 200 mL of acidic bath without and/or with different 2-(2-oxoindolin-3-ylamino)-5-phenyl-1,3,4-thiadiazole concentrations (blank, 0.05, 0.15, 0.25, and 0.50 mM), for 1, 3, 5, and 10 h.. The efficiency (IE, %) was estimated in accordance with equation 1:

$$IE\% = \left(1 - \frac{w_2}{w_1}\right) \times 100 \qquad \mathbf{1}$$

Quantum Chemical Calculation

Quantum chemical simulations were performed through the Austin Model 1 (AM1) method. The simulations for the molecular structure of 2-(2-oxoindolin-3-ylamino)-5-phenyl-1,3,4-thiadiazole were also optimized geometrically.

Statistical Analysis

Results are shown as the means ± standard deviations (SDs). The statistical significance of variations were carrying out through (**ANOVA**) using the statistical software SPSS 17.0 . Variations were considered important at $P < 0.05$, and the results were displayed as the means ± SDs (n = 3).

Results and Discussion

The organic inhibitor was prepared through the refluxation reaction mixture of indoline-2,3-dione and 5-amino-2- phenyl-1,3,4-thiadiazol. The sequence of the reaction formation of this compound is shown in Figure 1.

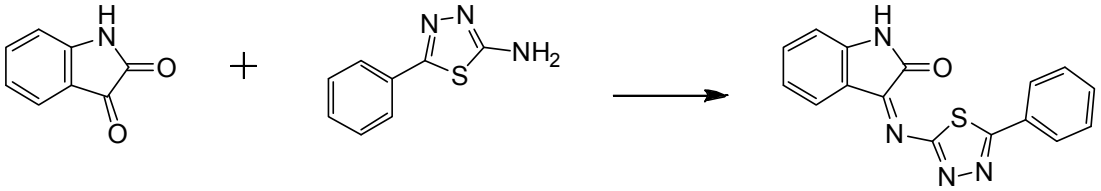

Figure 1. Chemical structure of the prepared corrosion inhibitor

Effect of Concentration

Figure 2 shows the change in corrosion rate with time during the corrosion of mild steel in HCl solution at 303 K. The corrosion rate of mild steel decreased linearly with time. This result suggests that the increasing efficiency of the inhibition of MS corrosion in HCl with time. Meanwhile, Figure 3 illustrates the changes in efficiency of the inhibition of MS corrosion in HCl (1 M) by different concentrations of inhibitor used as inhibitor. The addition of inhibitor remarkably lowered the weight loss relative to the weight at 0 M concentration. Hence, the inhibitor retarded the corrosion of MS in HCl.

As shown from Fig. 2 that corrosion rates diminish while the inhibition performance increased regarding to concentrations of inhibitor increased. However, the performance of inhibition of inhibitor suggesting a best inhibitive abilities towards corrosion. It is shown that the maximum efficiency reaches 71%.

Assessment of the postulated results showed that performance of inhibition of the studied molecules increments with raising of concentrations. It is credited due to raising the active surface performance (IE%/100). The highest value of performance of inhibition, of 71% were acquired at 0.5 mM concentration for investigated inhibitor. Furthermore, the concentration of inhibitor that increased would not issue any significant change in the impedance performance and showing that 0.5 mM is ideal concentration for the studied inhibitor. The inhibition performance of studied inhibitor can be showed impute to presence of the thiadiazole attached to the benzene ring. The best inhibition achievement of the studied inhibitor was imputing to presence of resonance effects. The unshared electron pairs in studied inhibitor molecules increase the resonance capability and thus increase the inhibition performance.

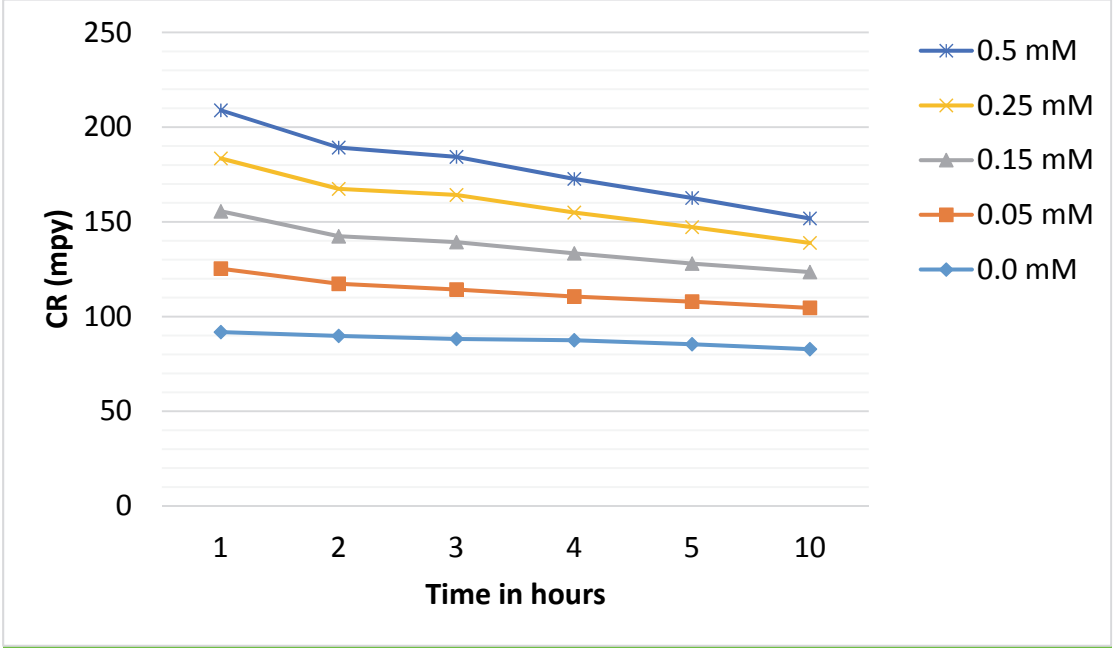

Figure 2. Effect of inhibitor concentrations on corrosion rate at various time points.

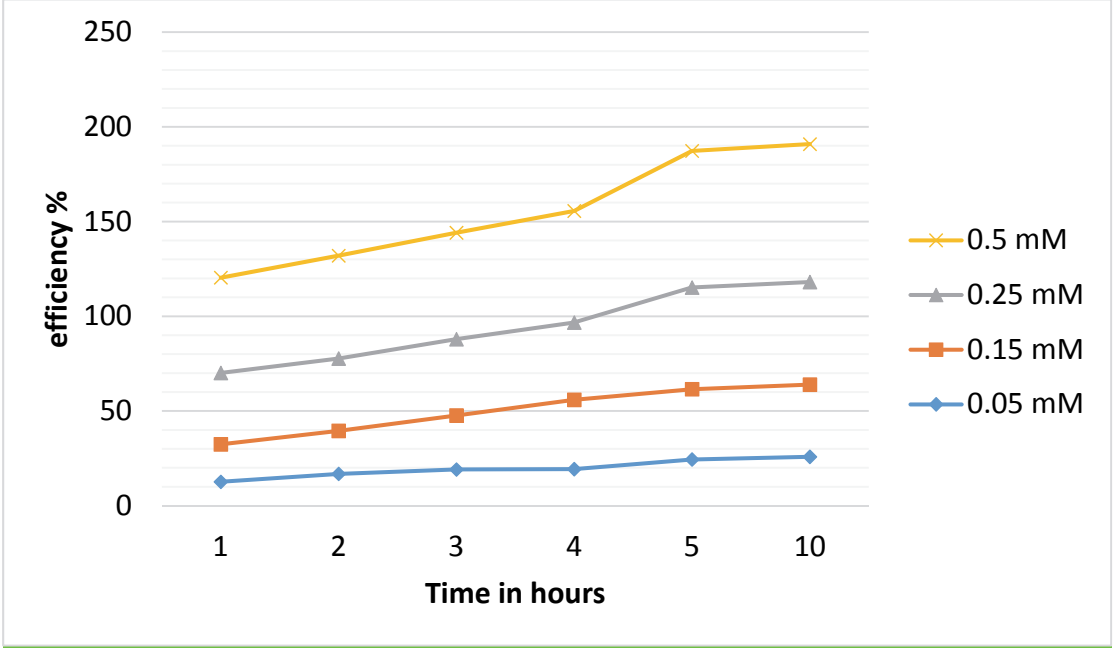

Figure 3. Effect of various PTIO concentration with various time points at 303 K.

Effect of Temperature

Temperature considerably affects corrosion. In general, corrosion rates increased with the increasing of temperature. This study investigated the impact of temperature on the anti-corrosion activities. Weight-loss techniques were performed at the temperature range 303–333 K in the absence and presence of various concentrations of inhibitor used as inhibitor. The obtained data are displayed in Figure 4.

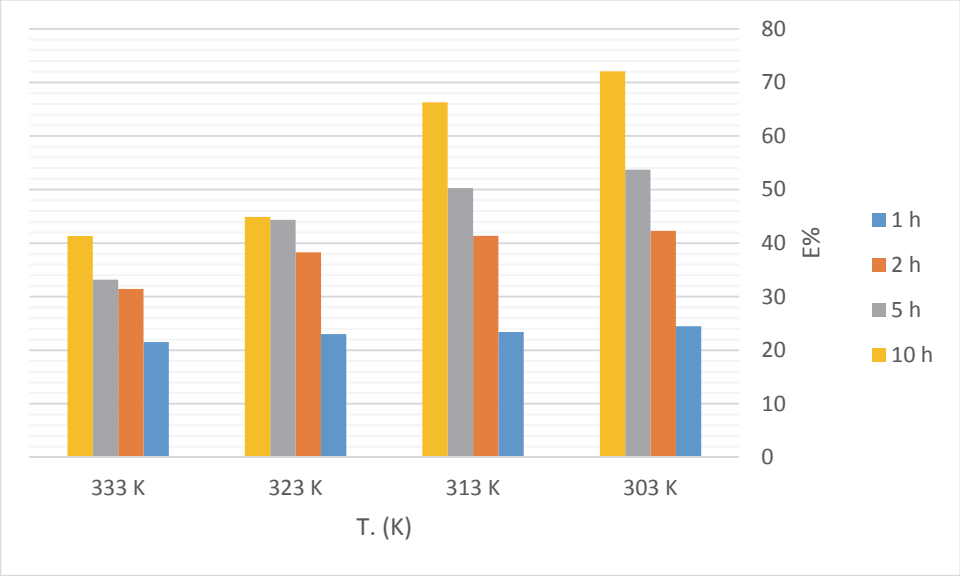

Figure 4. Temperature impact on the corrosion-inhibition efficiency of used PTIO with various concentrations.

The obtained results from our investigation imply that the corrosion rate raise in parallel with temperature in the utilized corrosive solutions in presence and absence of corrosion inhibitor especially without inhibitor. This result signalize that the presence of inhibitor goes to diminution the corrosion rate. Furthermore, we observe that the inhibition efficiency be based at room temperature and diminution, with the increasing of temperature. The inhibition efficiency become has best value of 71 % in 1 M of corrosive solution at 303 K, that explain superior, inhibitive performance of PTIO as corrosion inhibitor. The diminution in inhibition efficiency regarding to raising temperature might be refer to the increased desorption of PTIO molecules from surface of the metal and the raising in the protective film solubility and/or the reaction products precipitated on the mild steel surface which may further block the reaction

Temperature played an important role in the inhibition efficiency of mild steel in hydrogen chloride environment. The inhibition efficiency reached lowest value at 303 K, then gradually diminish obviously regarding to temperature. The decreasing of inhibition efficiency was generally due to the decomposition of the inhibitor molecules. Moreover, corrosion film may have further dominant role in the diminish in corrosion rate than the decreasing of proton concentration.

SEM

SEM of examined samples in 1 M corrosive acidic media without or with of inhibitor (0.5 mM) is displayed in Figure 5. The mild steel coupon surface was smooth, which indicates the absence of corrosion. On the contrary, the surface of the mild steel coupon inundated with corrosive solution (1 M HCl) without PTIO became relatively rugged due to metal decay. However, the presence of inhibitor decreased the corrosion rate and prevented surface damage. This observation indicates the formation of a protective layer on the samples.

With Inhibitor

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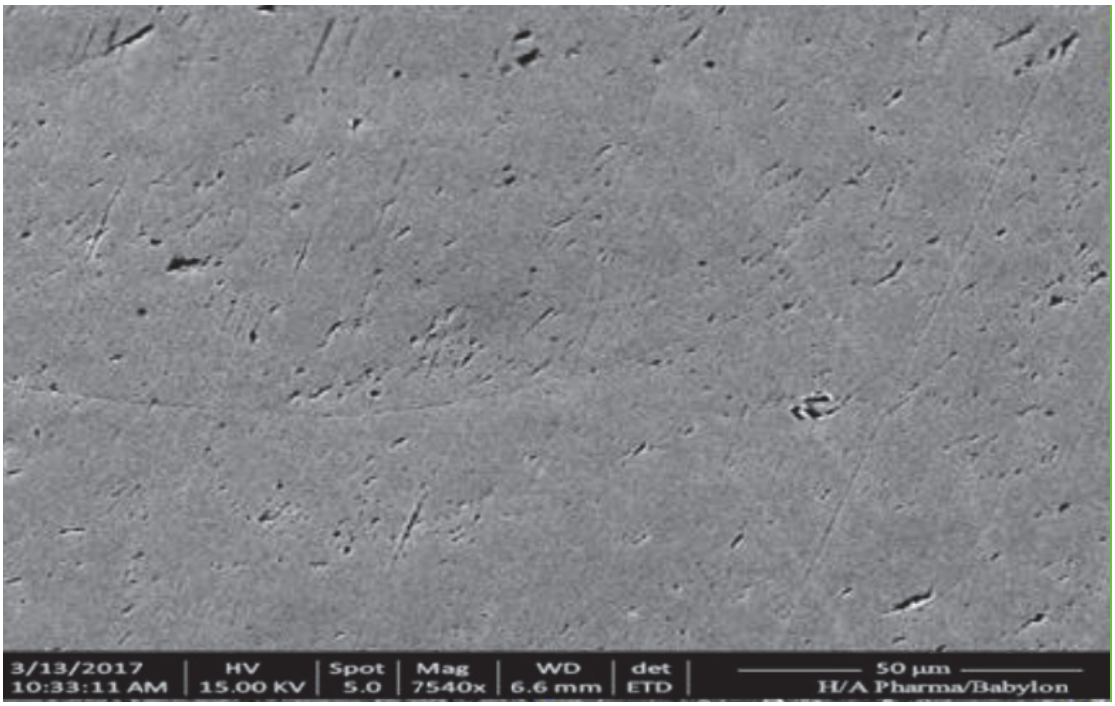


Without Inhibitor

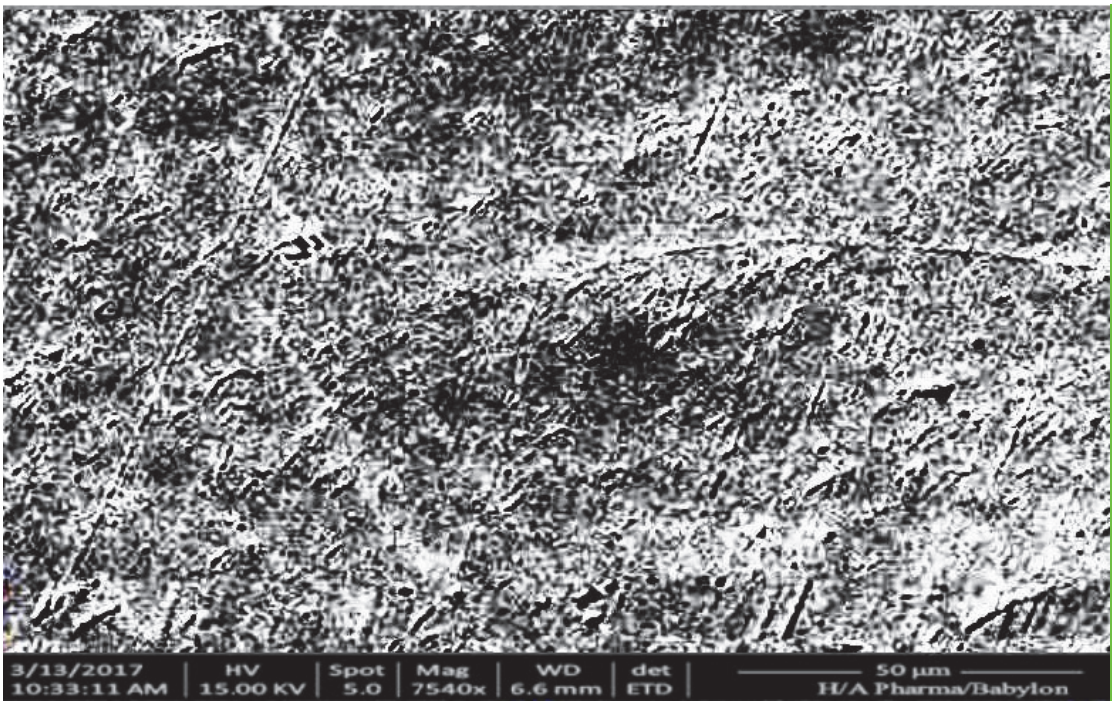


Figure 5. SEM images of the mild steel in HCl (0.5 mM) at 30 °C for 5 h.

Quantum Chemical Calculation

AM1 has been applied to correlate the corrosion-inhibition efficiency of inhibitor and its molecular structure (Figure 6). Table 1 lists the quantum parameters calculated through the AM1 semiempirical method [30]. The calculated parameters mainly included the highest

occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (ELUMO) (Figure 7), dipole moment (μ), and total energy. The energy of the HOMO was associated with the capability to donate electrons for inhibitor molecules; the inhibition efficiencies increased with increasing energy of the HOMO. The EHOMO indicates that the PTIO molecules tended to donate electrons to the metal with low-energy unoccupied orbitals. The highest EHOMO value of the inhibitor molecules transport by the adsorbed layer. The calculated parameters are shown in Table 1 with the average experimental efficiencies.

Table 1 Quantum chemical parameters of PTIO calculated using Austin Model 1 method

Energy (kcal/mol)	EHOMO (eV)	ELUMO (eV)	Dipole moment (μ)
79.8564	−7.771	-4.520	2.93

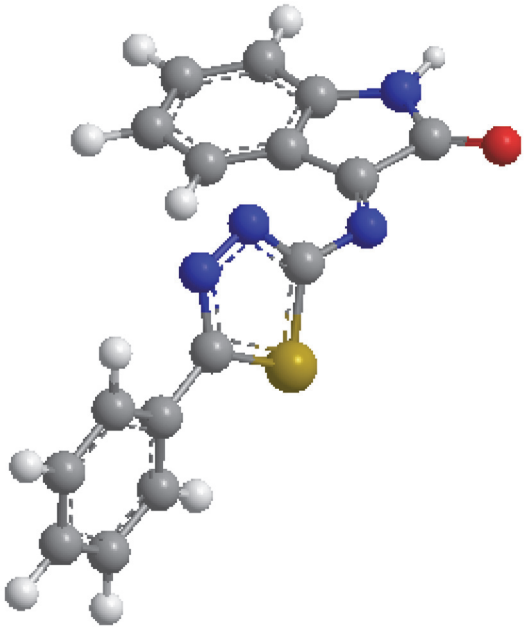
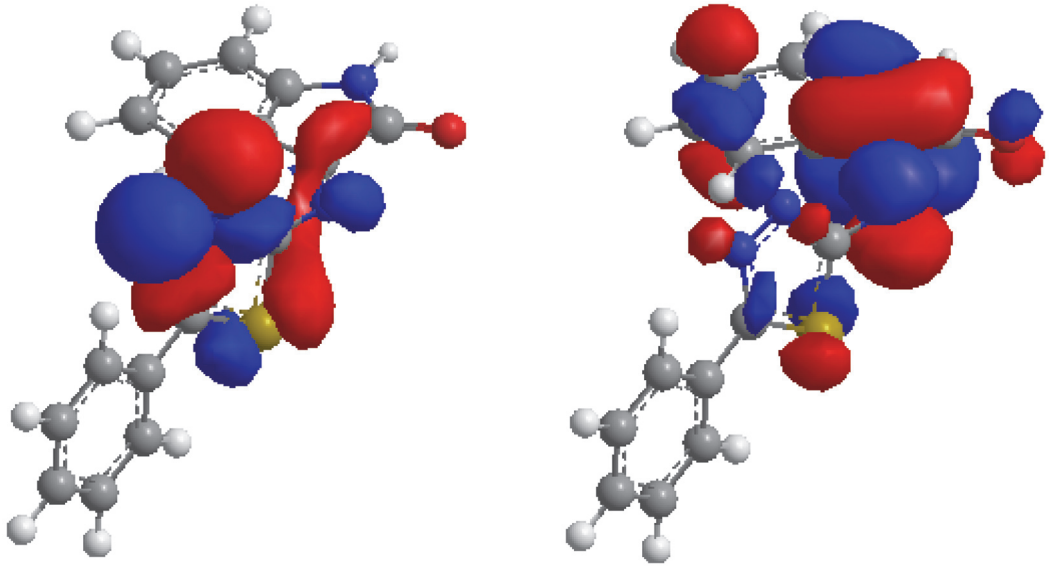


Figure 6. Optimized structure of PTIO.



HOMO LUMO

Figure 7. HOMO and LUMO structures of PTIO**.**

Mechanism of inhibition

Corrosion control is carried out via realizing and recognizing corrosion mechanism through utilizing corrosion inhibitive metal. The results exhibit that the mechanism of inhibition involves block the surface of mild steel by molecules of PTIO molecules through Langmuir process of adsorption and the nitrogen, sulfur and oxygen plays a significant role in the inhibition performance of the PTIO inhibitor.
The inhibitory impact of the inhibitor investigated the adsorption behavior and inhibition mechanism on the surface of mild steel through quantum chemistry. It was found that the inhibitor molecules demonstrated ability to donate electrons to the metal and formation coordination bonds.

Conclusions

The inhibitor was synthesized successfully with remarkable yield and structure was illustrated through spectroscopics techniques in addition to elemental analysis. This inhibitor displayed an excellent inhibitory effect on the corrosion of mild steel in hydrochloric acid solution as the corrosive bath. Weight-loss measurements showed that the inhibition effect increased with increasing concentrations of inhibitor. Quantum calculations implied that the nitrogen, oxygen, and sulfur atoms of the synthesized inhibitor were the most active adsorption sites that interacted with the mild steel surface to form a film. Furthermore, a correlation was noted between the quantum calculations for PTIO and the metal surfaces.

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