

Full Paper

Effect of a New Synthesized Schiff base Containing Thiophene Rings on Carbon Steel Corrosion in HCl Solution

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Abstract- In the present work, the corrosion of carbon steel in 1.0 molL⁻¹ HCl was investigated in the presence of new synthesized inhibitor, 2-methyl-N'-(di(thiophen-2-yl)methylene)benzohydrazide (DTBH) by Potentiodynamic polarization (PDP), Electrochemical Impedance Spectroscopy (EIS) and Weight Loss (WL) measurements. Polarization studies showed that DTBH acted as a mixed-type corrosion inhibitor with predominantly anodic inhibition effect. EIS results confirmed the adsorptive type of the inhibitor, which increased the polarization resistance of the corrosion reaction. Based on the weight loss results, maximum inhibition efficiency was obtained 92.0% at the concentration of 300 ppm of DTBH. It was also shown that the adsorption of DTBH obeys Langmuir isotherm with mainly chemisorption.

Keywords- Carbon steel, Corrosion inhibition, Adsorptive inhibitor, Schiff base

1. INTRODUCTION

Corrosion, in the most common use of the word, is the destruction of metals by interaction with environment and a loss of their electrons. Corrosion is an undemand process that imposes economic disadvantages or safety problems to various industries. So, investigation of corrosion

control methods is a significant research field having enormous practical importance. One of the most cost-effective ways to control corrosion is using corrosion inhibitors. Corrosion inhibitors are chemicals that are added to a chemical environment to prevent or decelerate corrosion so that the metal under protection will have a longer lifetime [1,2]. The major industries using corrosion inhibitors are oil and gas exploration, petroleum refining, chemical manufacturing, water treatment and the product additive industries [1,3-5]. Regarding their electrochemical mechanism of corrosion inhibition, the inhibitors divided into three groups: cathodic, anodic and mixed-type or adsorptive inhibitors [1,6].

Carbon steel is generally used in most of the chemical industries due to its low cost, easy availability and good strength. So, corrosion of carbon steel is a serious problem in aggressive environment and needs to be controlled. As stated above, one of the effective strategies against corrosion is adding corrosion inhibitors to the corrosive medium. Currently, studying on development new low-cost and low-toxic inhibitors for carbon steel takes increasing considerations [7-12]. Usually, presence of heteroatoms N, S, or O and π -electrons in the form of conjugation in organic substrate leads to acting as a corrosion inhibitor [8-14]. Schiff bases with the general structure $R_2C=NR'$ ($R' \neq H$) are typically formed by condensation of a primary amine and an aldehyde [15]. Due to their advantages such as low cost, easy formation, versatility and complex formation ability, Schiff bases have increasing applications in various fields [16-18]. Regarding their ability to cover the metal surface by forming a protective monolayer, they also can be used as effective corrosion inhibitors [19-24]. In this work, the effect of a newly synthesized Schiff base on carbon steel corrosion was investigated in HCl solution. HCl is an important inorganic acid especially in pickling baths to remove rust or scale from iron or steel before subsequent steps [25,26]. As shown in Fig. 1, the studied inhibitor contains a benzohydrazide moiety and two thiophen rings. The corrosion inhibition studies were done by potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS) and weight loss (WL) measurements.

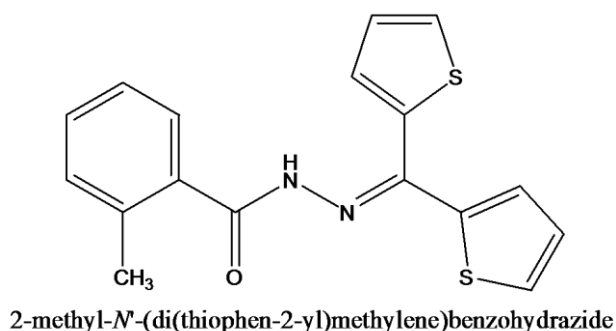


Fig. 1. Molecular structure of the studied inhibitor (DTBH)

2. EXPERIMENTAL

2.1. Materials and solutions

The inhibitor DTBH was synthesized by the reaction between 2-methylbenzohydrazide and di(thiophen-2-yl)methanone according to the previously described procedure [14]. The corresponding synthesis reaction is represented in Fig. 2.

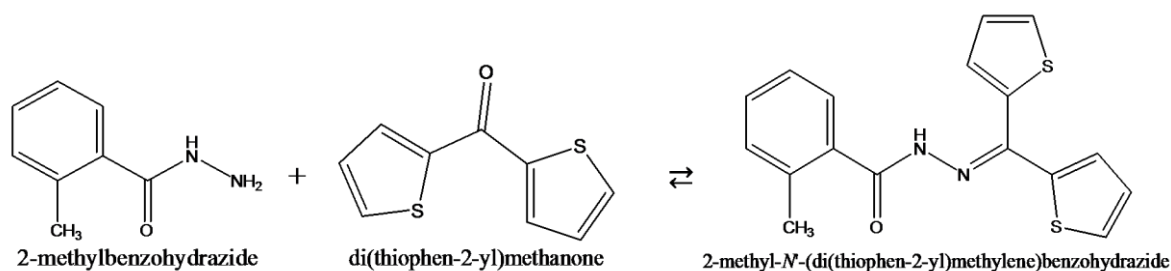


Fig. 2. Synthesis reaction of DTBH

To solve the solubility problems, the inhibitor solutions were prepared in 1.0 molL^{-1} HCl containing 5% v/v dimethyl sulfoxide (DMSO). This volume of DMSO was also added to the blank solution. The blank solution was prepared by dilution of 36% HCl (from Merck) to concentration of 1.0 molL^{-1} with distilled water.

All corrosion tests were done using carbon steel containing C 0.693%, Si 0.043%, Mn 1.050%, P 0.069%, Cr 0.058%, Ni 0.074%, Al 0.036%, S 0.290%, Cu 0.167%, V 0.004%, W 0.001%, Mo 0.0143% and the balance iron. Before doing each experiment, carbon steel surface was abraded by different grades of emery papers (400-1200), degreased and cleaned in an ultrasonic bath with ethanol and acetone, and finally rinsed with distilled water.

2.2. WL experiments

WL measurements were carried out with abraded, cleaned and dried carbon steel sheets of $5.0 \text{ cm} \times 2.5 \text{ cm} \times 0.2 \text{ cm}$, which were accurately weighted with a sensitivity of $\pm 0.1 \text{ mg}$ at 298 K. The cleaned specimens were immersed in 100 mL of 1.0 molL^{-1} HCl in the absence and presence of various concentration of DTBH. After 6 h immersion, the specimens were taken out from the solution, cleaned, dried and finally accurately reweighed. The measurements were performed in triplicate and the average values were reported.

2.3. Electrochemical experiments

Electrochemical experiments were done using an AUTOLAB model PGSTAT30 containing a frequency response analyzer with a three-electrode set-up, which comprised a Pt

counter electrode (CE), an Ag/AgCl reference electrode (RE) and a carbon steel working electrode (WE). The working electrode was made by mounting a cylindrical carbon steel bar in epoxy resin to get an exposed surface area of 1.0 cm^2 . Before doing each experiment, the fresh surface of WE was immersed in the test solution for 45 min to reach a relative steady state and found open circuit potential (E_{ocp}). Potentiodynamic polarization curves were recorded by sweeping the potential from a more positive to a more negative value than E_{ocp} at a scan rate of 1 mV/S .

EIS measurements were carried out at E_{ocp} by superimposing a sinusoidal potential of 5 mV amplitude at frequencies between 1.0×10^5 - $1.0 \times 10^{-2} \text{ Hz}$. Electrochemical data were recorded using a personal computer connecting to the electrochemical instrument. The obtained plots were analyzed using NOVA2.1 software. All experiments were done at 298 K .

3. RESULTS AND DISCUSSION

3.1. PDP measurements

PDP experiments were done for carbon steel electrode at the potential range containing E_{ocp} . The polarization results for carbon steel electrode in $1.0 \text{ molL}^{-1} \text{ HCl}$ without and with different concentrations of DTBH are shown as Tafel plots in Fig. 3. The figure shows that the corrosion current density decreases by adding DTBH to the corrosive solution, showing the inhibition effect of DTBH on the carbon steel corrosion.

The electrochemical parameters, which are extracted from Tafel plots are listed in Table 1. The inhibition efficiency values are calculated using the following equation [27-29]:

$$\eta\% = \frac{I_{\text{corr, uninhibit}} - I_{\text{corr, inhibit}}}{I_{\text{corr, uninhibit}}} \times 100 \quad (1)$$

In this equation, the $I_{\text{corr, uninhibit}}$ and $I_{\text{corr, inhibit}}$ denote the corrosion current densities without and with the inhibitor, respectively. As the data in Table 1 shows, with increasing the inhibitor concentration, the corrosion current density decreases and consequently, the inhibition efficiency increases. The maximum inhibition efficiency is obtained at the concentration of 300 ppm and equals 91.8% . Moreover, Fig. 3 and Table 1 revealed that the addition of DTBH to the solution causes Tafel plot to shift toward more positive potentials. The maximum shift was observed for the solution containing 300 ppm of DTBH ($E_{\text{corr}} = -510 \text{ mV}$), which equals 8 mV toward anodic potentials. So, according to literatures, the inhibitor can be considered as adsorptive or mixed-type corrosion inhibitor with predominantly anodic inhibition effect [14,30,31]. Table 1 also shows a slight change in both anodic and cathodic Tafel slopes due to the inhibitor addition. This observation reveals that the inhibitor DTBH hinders carbon steel corrosion by shielding the anodic and cathodic sites of the corrosion reaction. So, the mechanism of corrosion reaction does not change [21,31,32].

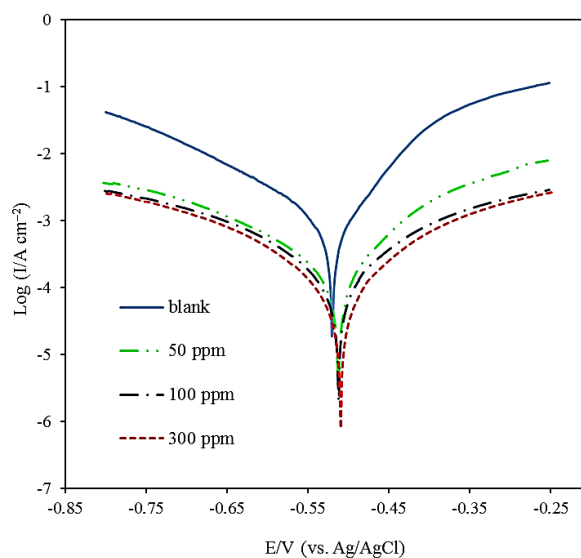


Fig. 3. Polarization curves for carbon steel electrode in 1.0 molL^{-1} HCl without and with different concentrations of DTBH with a scan rate of 1 mVs^{-1}

Table 1. Polarization parameters and the corresponding $\eta\%$ values for carbon steel corrosion in 1.0 molL^{-1} HCl in the absence and presence of various concentrations of DTBH

Inhibitor	C_{inh} (ppm)	$-E_{\text{corr}}$ (mV)	I_{corr} ($\mu\text{A cm}^{-2}$)	$-b_c$ (mV dec $^{-1}$)	b_a (mV dec $^{-1}$)	η (%)
Blank	0	518	802.1	123	93	-
DTBH	50	512	140.4	124	94	82.5
	100	512	109.1	125	93	86.4
	300	510	65.8	128	96	91.8

3.2. EIS results

The inhibition behavior of DTBH on carbon steel corrosion in 1.0 molL^{-1} HCl was also studied by EIS, which is a useful tool for investigating the corrosion inhibition processes. EIS provides information on both the resistive and capacitive behavior at metal /surface interface. Fig. 4 shows the impedance spectra as Nyquist plots for carbon steel electrode in 1.0 molL^{-1} HCl in the absence and presence of different concentrations of DTBH. For both inhibited and uninhibited solutions, Nyquist plots have one depressed semicircle, indicating that one charge transfer process controls the carbon steel corrosion reaction. As the figure shows, the diameter of the semicircle in the presence of DTBH is larger than that without DTBH and increases with increasing the inhibitor concentration. This observation shows the increase in charge transfer resistance, which results from the inhibition effect of DTBH. The electrical equivalent circuit of the system is shown in Fig. 5, in which R_s , R_p , and CPE symbolize the solution resistance, the polarization resistance and constant phase element, respectively [33-35]. CPE is substituted

for capacitor to give a more accurate fit to account for the depressed shape of the semicircles, coming from the inhomogeneity of the electrode surface [36,37]. The impedance of CPE element is given by the following equation [38]:

$$Z_{\text{CPE}} = \frac{1}{Y_0(j\omega)^n} \quad (2)$$

where Y_0 is the magnitude of the CPE, j is the imaginary number, ω is the sine wave angular frequency ($\omega=2\pi f$, the frequency in Hz) and $-1 \leq n \leq 1$ is the phase shift, which gives information on the degree of surface inhomogeneity. CPE can be considered as a resistor if $n=0$, a capacitor if $n=1$ or an inductor if $n=-1$. Fitted results for impedance parameters obtained from Nyquist plots in Fig. 4 are shown in Table 2. Equation 3 [39] was used to calculate the values of $\eta\%$ in Table 2:

$$\eta\% = \frac{R_{p,\text{inhibit}} - R_{p,\text{uninhibit}}}{R_{p,\text{inhibit}}} \times 100 \quad (3)$$

In this equation, $R_{p,\text{inhibit}}$ and $R_{p,\text{uninhibit}}$ are the polarization resistances of inhibited and uninhibited solutions, respectively.

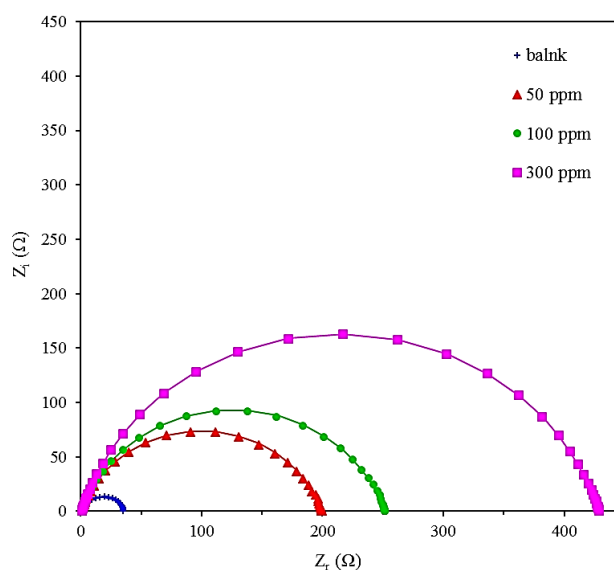


Fig. 4. Nyquist plots of carbon steel electrode obtained in 1.0 molL^{-1} HCl in the absence and presence of various concentrations of DTBH. Solid lines show fitted results

Table 2 shows that R_p values increase with increasing the inhibitor concentration, which is caused by adsorption of DTBH species and formation a protective layer on carbon steel surface. This protective film leads to an expansion in the electrical double layer and a decrease in the CPE magnitude [14,40]. The slight increase in n values with increasing the inhibitor concentration indicates that the inhibitor addition slows the corrosion reaction down and so,

the surface remains smoother. However, no substantial change is observed in the value of n in the absence and presence of the inhibitor, indicating that the mechanism of the corrosion reaction in 1.0 molL^{-1} HCl does not change with the inhibitor addition [10]. Based on EIS results, the maximum inhibition efficiency was 91.8% and obtained for the solution containing 300 ppm DTBH.

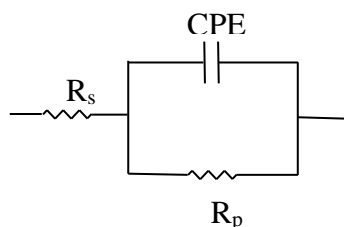


Fig. 5. Electrical equivalent circuit used for fitting EIS data

Table 2. Electrochemical impedance parameters for carbon steel electrode in 1.0 molL^{-1} HCl in the absence and presence of various concentrations of DTBH

Inhibitor	C_{inh} (ppm)	R_p ($\Omega \text{ cm}^2$)	n	Y_0 ($\mu\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$)	η (%)
Blank	0	35.2	0.81	313.3	-
DTBH	50	197.8	0.82	65.5	82.2
	100	250.2	0.82	53.7	85.9
	300	427.6	0.83	32.6	91.8

3.3. Weight loss measurements

Carbon steel corrosion rate (CR) after 6 h exposure to 1.0 molL^{-1} HCl without and with different concentrations of DTBH were calculated according to the following equation [41]:

$$CR = \frac{W_0 - W_t}{S \cdot t} \quad (4)$$

where W_0 and W_t are the mass values of carbon steel sheet before and after immersion in the HCl solution (mg) respectively, S denotes the specimens total area (cm^2), t is the exposure time (h) and CR is the corrosion rate ($\text{mgcm}^{-2}\text{h}^{-1}$). The values of surface coverage (θ) and $\eta\%$ were calculated as below [41]:

$$\theta = \frac{CR_{\text{uninhibit}} - CR_{\text{inhibit}}}{CR_{\text{uninhibit}}} \quad (5)$$

$$\eta\% = \frac{CR_{\text{uninhibit}} - CR_{\text{inhibit}}}{CR_{\text{uninhibit}}} \times 100 \quad (6)$$

In these equations, $CR_{uninhibit}$ and $CR_{inhibit}$ represent the values of carbon steel corrosion rates in uninhibited and inhibited HCl, respectively. Table 3 lists the values of CR, θ and $\eta\%$ after 6 h immersion in HCl solutions in the absence and presence of different concentrations of DTBH at 298 K.

The data in Table 3 shows that the corrosion rate of carbon steel reduced with the addition of DTBH to the aggressive solution. The inhibition efficiencies increased with increasing the inhibitor concentration, which indicates that the surface coverage also increased. The maximum inhibition efficiency (92.0) was obtained at the presence of 300 ppm of DTBH.

Table 3. Weight loss results of carbon steel corrosion in 1.0 molL^{-1} HCl in the absence and presence of various concentrations of DTBH at 298 K

Inhibitor	C_{inh} (ppm)	CR (mpy)	θ	η (%)
Blank	0	373.6		-
DTBH	50	63.8	0.83	82.9
	100	50.9	0.86	86.4
	200	40.4	0.89	89.2
	300	29.9	0.92	92.0

3.4. Adsorption isotherm

As it was shown in electrochemical investigations, the studied inhibitor retarded carbon steel dissolution by adsorption on the metal surface. So, it would be valuable to study the mode of DTBH adsorption on carbon steel surface. Various adsorption isotherms were tested using WL data and the best fit was achieved with Langmuir isotherm. Fig. 6 shows the Langmuir adsorption plot for adsorption of DTBH on carbon steel in 1.0 molL^{-1} HCl at 298 K. As the figure shows, the values of linear correlation coefficient and slope are very close to 1, confirming the Langmuir mode of adsorption. The adsorption equilibrium constant k_{ads} can be calculated from the Langmuir adsorption equation [42,43]:

$$\frac{C_{inh}}{\theta} = \frac{1}{k_{ads}} + C_{inh} \quad (7)$$

where C_{inh} is the inhibitor concentration (molL^{-1}), k_{ads} is the adsorptive equilibrium constant (Lmol^{-1}) and θ is the surface coverage. The value of k_{ads} was calculated from the intercept of the line and equals $3.7 \times 10^4 \text{ molL}^{-1}$. The relatively high value of k_{ads} reveals high adsorption ability of the studied molecule on carbon steel surface. On the other hand, k_{ads} value can be used to calculate the value of the standard free energy of adsorption (ΔG_{ads}^0) using the following equation [42,43]:

$$\Delta G_{\text{ads}}^0 = -RT \ln 55.5 K_{\text{ads}} \quad (8)$$

where R is the universal gas constant ($8.314 \text{ JK}^{-1}\text{mol}^{-1}$), T is the absolute temperature (K) and 55.5 is the molar concentration of water in the solution (molL^{-1}). From Eq. (8), the value of ΔG_{ads}^0 was obtained -36.0 kJmol^{-1} . The negative sign of ΔG_{ads}^0 value indicates spontaneous adsorption of the inhibitor molecule on carbon steel surface [44]. On the other hand, the calculated value is in the range between 20 and 40 kJmol^{-1} , indicating that the adsorption process involves both chemisorption and physisorption [44,45]. However, the value of ΔG_{ads}^0 is more close to -40 kJmol^{-1} , which can be an evidence that the adsorption of DTBH takes place predominantly by chemisorption [10,45].

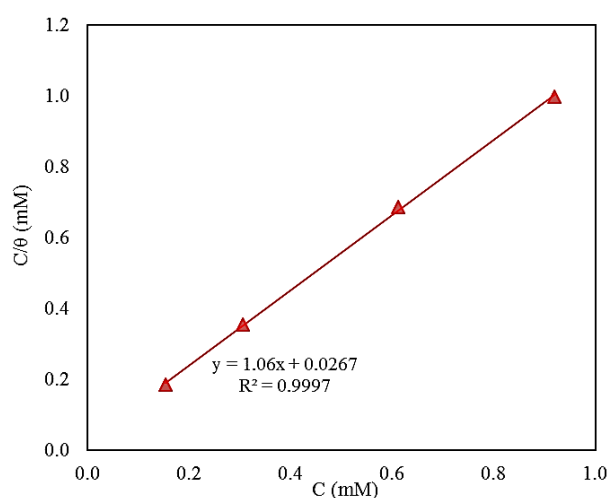


Fig. 6. Langmuir adsorption isotherm model for DTBH on carbon steel surface at 298 K

4. CONCLUSION

In this paper, a benzohydrazide Schiff bases, DTBH, was studied as carbon steel corrosion inhibitor in 1.0 molL^{-1} HCl. Potentiodynamic polarization studies showed that DTBH acted as a mixed type corrosion inhibitor. On the EIS spectra, one capacitive loop was observed in the absence and presence of the inhibitor. The radius of the observed semicircle increased with the inhibitor concentration, indicating that the R_p of the corrosion reaction increased due to adsorption of the inhibitor molecules on carbon steel surface to form a protective barrier. WL results also confirmed the electrochemical results and showed that the maximum inhibition efficiency (92.0%) was obtained with 300 ppm of DTBH. Adsorption of DTBH obeys Langmuir isotherm with relatively large value of K_{ads} that indicates the strong adsorption of DTBH on the metal surface.

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