Corrosion inhibition of thiadiazole derivative for mild steel in hydrochloric acid solution

R.D. Salim,1 Q.A. Jawad,2,3 K.S. Ridah,3 L.M. Shaker,3 A.A. Al-Amiery,3* A.A.H. Kadhum4 and M.S. Takriff5

1Department of Machinery Equipment Engineering Techniques, Technical College Al-Musaib, Al-Furat Al Awsat Technical University, Al-Musaib, Babil 51009, Iraq
2Electrical Engineering Department, University of Technology, Baghdad 10001, Iraq
3Energy and Renewable Energies Technology Center, University of Technology, Industrial Street, Baghdad 10066, Iraq
4University of Al-Ameed, Karbala, Iraq
5Department of Chemical & Process Engineering, Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia, Bangi, Selangor 43600, Malaysia
E-mail: dr.ahmed1975@gmail.com

Abstract

In the various industries such as pickling, gas and oil industries in which an acid medium, especially hydrochloric acid, is used, the corrosion of mild steel significantly increases destruction with a huge financial loss. The best method for preventing corrosion of mild steel alloy is to use an impermeable layer over the target alloy. The coatings are not constantly impervious, and all coating techniques finally fail for various reasons and therefore, anti-corrosion agents are added. The inhibition impact of new corrosion inhibitor entitled “5,5’-(1,4-phenylene)bis(N-benzylidene-1,3,4-thiadiazol-2-amine)” (PBTA) on the surface of mild steel corrosion in 1 M HCl media was studied using weight loss techniques. The surface of mild steel was exposed to investigated solution and evaluated using scanning electron microscopy (SEM). Effects of the concentration of PBTA, acidic content, temperature variation and immersion time were investigated. PBTA has excellent inhibitive performance on the corrosion of mild steel in 1 M HCl solution and enhanced with an increase in PBTA inhibitor concentration, while decreasing with a decrease in immersion time and corrosion temperature. The adsorption of the synthesized corrosion inhibitor on the surface of mild steel obeys the Langmuir adsorption isotherm. Various spectroscopic techniques such as 1H NMR (Proton nuclear magnetic resonance), 13C NMR (Carbon-13 nuclear magnetic resonance) and FTIR (Fourier-transform infrared) were used for confirmation of the structure of the corrosion inhibitor molecule.

Keywords: mild steel, PBTA adsorption isotherm, weight loss, inhibitor.

Introduction

Corrosive solutions are used on a larger scale to remove unwanted oxides in boilers cleaning, metalworking and heat exchangers. For this reason, the extremely corrosive nature of hydrochloric acid (HCl) should be limited through the appropriate corrosion inhibitors [1–7]. From recent studies, the superior inhibitors that have the ability to adsorption on alloy surface should contain a hetero-atom in their chemical structure like oxygen, nitrogen and phosphorus in addition to some π-bonds [8–13]. According to the literature, considerable compounds which have nitrogen and sulfur have been studied as corrosion inhibitors and found to be excellent corrosion inhibitors [14, 19]. It is obvious that these inhibitors perform as mixed-type compounds, their performance increases with the immersion time. Thus, nitrogen and sulfur compounds inhibition features are notarized to their electrons pairs of in sulfur and nitrogen. Furthermore, numerous oxygen, sulfur, phosphorous and nitrogen compounds are considered as drugs [20, 23].

Adsorption of natural and organic molecules depends particularly on the electronic structures and the inhibition performance increases with the number of aromatic rings [25, 28]. Eventually, adsorption of these compounds on alloy surface is associated to chemical structure and charge density [29–34]. The main thematic of this investigation was to synthesize and study the effect of new corrosion inhibition of PBTA molecules on mild steel corrosion in 1.0 M HCl using weight loss technique and scanning electron microscopy analysis (SEM). Also, the effect of immersion time and temperature variation on PBTA activity was investigated.

Experimental

Materials, inhibitor synthesis and samples preparation

Benzaldehyde, terephthalic acid, thiosemicarbazide, absolute ethanol and other chemicals were from Sigma-Aldrich company, Malaysia, and used without further purification. The 5,5′-(1,4-phenylene)bis(N-benzylidene-1,3,4-thiadiazol-2-amine) (PBTA) used as corrosion inhibitor in the study was obtained by reflux of the reaction mixture of 0.15 mol terephthalic acid and 0.30 mol thiosemicarbazide. Then, the mixture was stirred in 50 ml of sulfuric acid for 7 hours in a round bottomed flask. After the chemical reaction being completed, the reaction mixture was cooled down and poured into ice water. The prepared mixture was basified by employing an ammonium hydroxide concentrated solution. In addition, PBTA product was precipitated and filtered, then the crude product was achieved. PBTA was recrystallized from 10–15% aqueous ethanol. The pure prepared product was dried under vacuum over phosphorus pentoxide for 24 hours. A mixture of PBTA and benzaldehyde (0.01 mol of each) was refluxed for 90 min in 30 ml of absolute ethanol and then left for cooling in ice water. The solid material was filtered and washed with 2% HCl, then recrystallized from ethanol twice to yield 39% of PBTA; m.p. 167–171°C. FTIR spectra were done by Shimadzu 8300 spectrometer. FT-IR (cm⁻¹); 3140 (C–H aromatic) and 1575 (C=N). NMR spectra were recorded by a Bruker
Spectrospin instrument equipped with 400 MHz Ultra Shield using TMS as internal standard. $^1$H NMR in d$_6$-DMSO; d: 8.68 ppm (1H, CH) and d: 7.49–7.81 (C–H, Ar). $^{13}$C NMR in d$_6$-DMSO: 127.87, 128.41, 129.74, 132.52, 136.11, 136.93, 167.18 and 173.73. CHN investigation was estimated utilizing Carlo Erba 5500 CHN elemental analyzer. CHN Analysis for PBTA; Found (Calculated): C, 63.11% (63.70); H, 4.01% (3.56); N, 18.06% (18.57). The structural formula of PBTA is given in Figure 1. PBTA was investigated as a corrosion inhibitor for mild steel in 1 M HCl acid.

The acid solution was used as the test solution and prepared from (37 wt.%) analytical grade HCl acid. The inhibited test solutions were 1 M HCl acid with addition of various concentrations of the inhibitor. The used mild steel samples each of 4.5 cm$^2$ active surface area were obtained from Gamry Instruments Inc. and were used as base substrates for gravimetric corrosion tests and were composed of (wt.%): 0.21 C, 0.05 Mn, 0.001 Al, 0.38 Si, 0.05 S, 0.09 P, and Fe balance. The specimens were well cleaned with the ASTM standard procedure G1-03 [35].

![Chemical structure of PBTA](image)

**Figure 1.** Chemical structure of PBTA.

An average value was calculated after repeating each measurement for three times. The immersion experiments were proceeded and carried out at 303, 313, 323 and 333 K temperature levels in water bath. The immersion duration time was used at 1, 5, 10, 24 and 48 h, respectively. Corrosion rate (CR) was calculated as (mm/y), inhibition efficiency (IE%) and the surface coverage (θ) can be calculated from Equations (1–3).

$$CR(\text{mm/y}) = \frac{KW}{ATD}$$

where $K$ is a constant (87.6); $A$ is the area (cm$^2$); and $D$ is the density (g/cm$^3$)

$$IE\% = \frac{W_0 - W_i}{W_0} \times 100$$

$$\theta = \frac{W_0 - W_i}{W_0}$$

$W_0$ and $W_i$ refer to mass loss of mild steel coupons in both of inhibitor absence and presence, respectively.

(Note: Equation 3 is only valid for inhibitors with blocking action).
Results and Discussion

Effect of PBTA concentration

The $CR$ and $IE(\%)$ plots versus PBTA inhibitor concentration (0.1–0.5) mM for an immersion time of 1, 5, 10, 24, 48 and 72 h in 1 M of HCl solution at 303 K are demonstrated in Figures 2 and 3. It can be noted that $CR$ decreases with increasing inhibitor concentration, but the corrosion inhibition performance is excellent to the PBTA concentration 0.5 mM and 5 h immersion. From the obtained results, molecules of PBTA inhibitor adsorb on mild steel surface, which in turn form a protective layer at high and low PBTA concentration. The variation of $CR$ and $IE(\%)$ with time of immersion is displayed in Figures 2 and 3. During the first 5 hours, a significantly large difference of $CR$ and $IE(\%)$ with the time of immersion was observed. Hence, the lowest value of $CR$ in the presence of PBTA reached 12.71%, while $IE$ reached its highest value of 94.10%.

Generally, inhibitor molecules adsorption rate is often a process of removal of water molecules adsorbed from metal surfaces called displacement reaction. It was assumed that PBTA molecules adsorption rate was higher than desorption rate during 5 hours (PBTA adsorption became saturated) and the adsorption layer formed on the metal surface to improve the anti-corrosion performance. In HCl solution, due to $Cl^-$ ions adsorption on metal surface, it acquired a negative charge. On the other hand, sulfur and nitrogen atoms of thiadiazole PBTA rings are easily protonated, this is attributed to the high electron density on it, thus positively charged species of inhibitors are formed. The adsorption process can exist between the positive inhibitor molecules and metal surface by electrostatic interaction. Furthermore, coordinate bond may be created between the unsharped $e^-$ pairs of non-protonated sulfur and nitrogen atoms of both PBTA molecules and metal surface. Moreover PBTA molecules may be adsorbed chemically because of the inhibitor $\pi$-electrons interaction with the metal surface. $IE(\%)$ does not improve significantly within immersion time prolonging attributed to raised desorption and reduced adsorption, this is because the molecules of protective inhibitor were incomplete and disorder to produce the local corrosion. $IE(\%)$ of PBTA generally depends on adsorption ability over the mild steel surface. The surface coverage ($\theta$) for various concentrations of PBTA is described as $IE/100$ and it is easy to be calculated from Equation 3 from weight loss technique.

Temperature impact

In order to investigate the PBTA action as a corrosion inhibitor at various temperature degrees, the weight loss measurements were carried out while keeping the time duration of immersion at 5 h in 1.0 M HCl solution with various concentrations of PBTA. $IE(\%)$ variation with changing temperature is illustrated in Figure 4, it is a good indication of $IE$ falling with temperature elevation due to the physical adsorption. This process can be explained because the time gap between adsorption and desorption processes of inhibitor molecules on metal surface begins to be shorter as the temperature increase. Hence, this
surface with an incomplete protective layer remains to be exposed to the acidic environment for a long period of time [36].

**Figure 2.** CR variation with various PBTA inhibitor concentrations at 303 K for different immersion duration times (h) in 1.0 M of HCl solution.

**Figure 3.** IE(%) variation with different PBTA concentration at 303 K for different immersion timed (h) in 1.0 M HCl solution.
Figure 4. IE(%) variation with an immersion time at different PBTA concentration and various temperature, at 5 h in 1.0 M HCl solution.

Scanning electron microscopy (SEM)

Mild steel surface morphology was noted and observed after 5 h immersion duration in 1.0 M HCl in existence and absence of PBTA inhibitor as illustrated in Figure 5. The presence of HCl acid media has a major role in making the corrosion in three dimensions, HCl media lead to deep damage of the mild steel surface as seen in Figure 5a. On account of the inhibitor adsorptive layers, it can be seen that the mild steel surface in the presence of PBTA molecules seems smooth (see Figure 5b), these layers prevent the utilized acid from penetration into the mild steel surface. This confirms the PBTA inhibition ability and its molecules generate the protective layers on the mild steel surface which in turn protect the metal surface from the corrosive HCl.

Figure 5. Mild steel surface morphology after 5 h of immersion in 1.0 M corrosive HCl: (a) without PBTA inhibitor; (b) in presence of 0.5 mM mild steel surface inhibitor.
**The adsorption isotherm**

Interaction between chemical molecules and alloy surface could be supplied through the adsorption isotherm. Various adsorption isotherms like Temkin, Freundlich and Langmuir were investigated in order to describe PBTA molecules adsorption behavior. As demonstrated in Figure 6, the best fit was the Langmuir isotherm, the obtained $C/\theta$ linear correlation coefficient ($R=0.9927$) and the straight line slope = 1.0382, it was close to the unity and that specified that PBTA molecules adsorption on the utilized mild steel surface were obeyed Langmuir model. To be specific, Langmuir adsorption isotherm characteristic is stated by Equation 4 [37, 38]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$$

Where the inhibitor concentration is denoted by $C$, the adsorptive equilibrium constant is denoted by $K_{ads}$ and $\theta$ value obtained from Equation 3. From Figure 6, $K_{ads}$ value can be calculated from intercept of the fitting formula.

![Graph](image-url)

**Figure 6.** Langmuir isotherm adsorption isotherm for PBTA in 1.0 M HCl solution.

The relation between $K_{ads}$ and the standard adsorption free energy ($\Delta G^0$) for Langmuir model can be demonstrated by Equation 5.

$$K = \frac{1}{C} \exp \left( -\frac{\Delta G^0}{RT} \right)$$

$R$ refers to the molar gas constant, $C$ is the concentration of water in solution and $T$ is the temperature in Kelvin.
From Figure 6, \((\Delta G^0)\) value has been estimated to be \(-37.728\) kJ/mol. The appeared negative sign proposed that the inhibitor molecules are adsorbed spontaneously on the metal surface. Generally, \((\Delta G^0)\) value of \(-20\) kJ/mol or lower signalize physisorption interaction however \(\Delta G^0\) value of \(-40\) kJ/mol or higher signalize chemisorption and the inhibitor molecules form coordinate bonds through transferring unpaired electrons from inhibitor molecules to the d-orbital of surface of metal [39]. In this work, \((\Delta G^0)\) value equal to \(-37.728\) kJ/mol. It was proposed chemisorption of PBTA because of heteroatoms existence (N and S) and N-containing heterocyclic conjugate system. Consequentially, potential reaction centers are unshared electron pairs on both hetero atoms and π-electrons of N-containing heterocyclic conjugate system. Particularly, –C=N group and –S existence in PBTA molecule is in favor of strongly adsorbed on metal surface in the acidic environment [40].

**Conclusion**

PBTA was successfully synthesized, chemically characterized by spectoscopical techniques in addition to CHN analysis and effectively improved the corrosion inhibition of mild steel in corrosive solution. PBTA as synthesized organic compound adsorbed strongly onto the mild steel, through electrostatic and coordination bonding. PBTA molecules built a protective layer on mild steel surface for blocking the reaction of corrosion and it worked as a cathodic type inhibitor. The adsorption of PBTA molecules on mild steel surface obeyed Langmuir adsorption isotherm. The results of weight loss and SEM are in good agreement.

**References**

5. A.A. Al-Amiery, A.A.H. Kadhum, A.B. Mohamad, A.Y. Musa and C.J. Li, Electrochemical study on newly synthesized chlorocurcumin as an inhibitor for mild


26. A.B. Mohamad, A.A.H. Kadhum, A.A. Al-Amiery, L.C. Ying and A.Y. Musa, Synergistic of a coumarin derivative with potassium iodide on the corrosion inhibition


★★★★