materials

Article

Novel Corrosion Inhibitor for Mild Steel in HCl

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Abstract: Corrosion inhibitory effects of new synthesized compound namely 5,5'-
((1Z,1'Z)-(1,4-phenylenebis(methanylylidene))bis(azanylylidene))bis(1,3,4-thiadiazole-2-thiol)
(PBB) on mild steel in 1.0 M HCl was investigated at different temperatures using open
circuit potential (OCP), potentiodynamic polarization (PDP) and electrochemical
impedance spectroscopy (EIS). Results showed that PBB inhibited mild steel corrosion in
acid solution and indicated that the inhibition efficiencies increased with the concentration
of inhibitor, but decreased proportionally with temperature. Changes in impedance
parameters suggested the adsorption of PBB on the mild steel surface, leading to the
formation of protective films.

Keywords: mild steel; thiadiazole; OCP; EIS; corrosion inhibition

1. Introduction

Corrosion is a common problem for steel and directly impacts its cost and safety [1]. The majority of
the well-known acid corrosion inhibitors are organic compounds that contain nitrogen, sulfur or oxygen
atoms [2]. Many organic compounds have been studied to investigate their corrosion inhibition potential,
e.g., the effect of organic nitrogen compounds on the corrosion behavior of iron and steel in acidic

solutions; these organic nitrogen compounds are usually employed for their rapid action [3,4]. Organic inhibitors can adsorb onto the metal/solution interface via four distinct mechanisms: (a) electrostatic attraction between charged molecules and the metal; (b) interaction between uncharged electron pairs in the molecule and the metal; (c) interaction between p-electrons and the metal and (d) a combination of mechanism (a) and (c) [5]. Generally, the tendency to form stronger coordination bonds and, as a result, the inhibition efficiency increases according to the following trend: O < N < S < P [6]. The planarity (p) and lone pairs of electrons present on N, O and S atoms are important structural features that control the adsorption of these molecules onto the surface of the metal [7]. Schiff bases are effective inhibitors for the corrosion of steel in acidic media [8]. Recent studies revealed that organic compounds containing polar functions groups would be quite efficient in minimizing the effect of corrosion in addition to heterocyclic compounds containing polar groups and π-electrons [9]. As a continuation of previous studies [10–14], we focused on the synthesis of new heterocyclic compounds as novel organic corrosion inhibitors. 5,5'-((1Z,1'Z)-(1,4-phnylenebis(methanylylidene))bis(azanylylidene))bis(1,3,4-thiadiazole-2-thiol) (PBB) was synthesized in intuition to be used as a corrosion inhibitor. PBB chemical structure was elucidated and confirmed using spectroscopic techniques (IR and NMR) in addition of elemental analysis. The molecular design of the new PBB is based on the fact that 1,3,4-thiadizole containing imine, mercapto and sulfide would contribute more effectively towards inhibition of corrosion of mild steel in acid medium. Structure for the newly synthesized corrosion inhibitor is shown in Figure 1.

Figure 1. Structure of PBB.
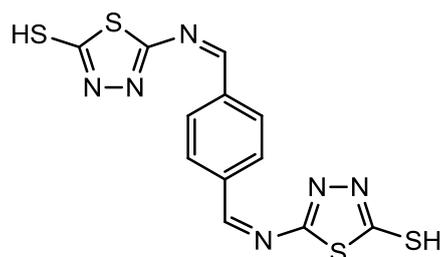
2. Results and Discussion

2.1. Synthesis of PBB

The reaction sequence for synthesis of PBB is outlined in Scheme 1 was followed. The starting material was 2-amino-5-mercapto-1,3,4-thiadiazole which is commercially available or, alternatively, readily accessible through cyclization of thiosemicarbazide with carbon disulfide in presence of potassium hydroxide. Synthesis of PBB was brought about by refluxing terephthalaldehyde with 2-amino-5-mercapto-1,3,4-thiadiazole (1:2) in the presence of few drops of hydrochloric acid.

The IR spectrum is good evidence for formation of synthesized PBB, like the absence of amine group at 3300–3190 cm^{-1}, and appearance new bands at 1694.7, 1608.5, 1560.04 cm^{-1}. In the IR spectrum of PBB, the imines stretching frequency were observed at 1608 and 1660 cm^{-1}. The high value of wave number for C=N was due to the high conjugation (resonance effect) for the substituted double bonds, whereas the aromatic carbon-carbon double bond stretching appeared at 1560 cm^{-1}. Although two types of tautomers, (thione and thiol) and (amine and imine), could be expected from the

PBB. The existence of the thiol form predominantly in the solid state is demonstrated by the presence of three absorption bands at 1694.7, 1608.5 and 1560.04 cm^{-1} belonging to the $\nu C=N$ groups, respectively and by absence of $\nu C=S$ and νNH. In the ^{1}H-NMR spectrum of PBB (Figure 2), a 2H singlet was observed at 8.068 ppm due to the imines protons and a 4H singlet at 7.270 ppm due to the aromatic protons. The isolated thiol proton was observed downfield as a 2H singlet at 3.500 ppm.

Scheme 1. Synthesis of PBB.
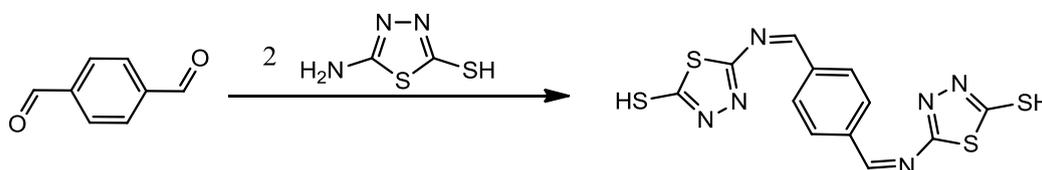
Figure 2. Proton NMR for PBB.
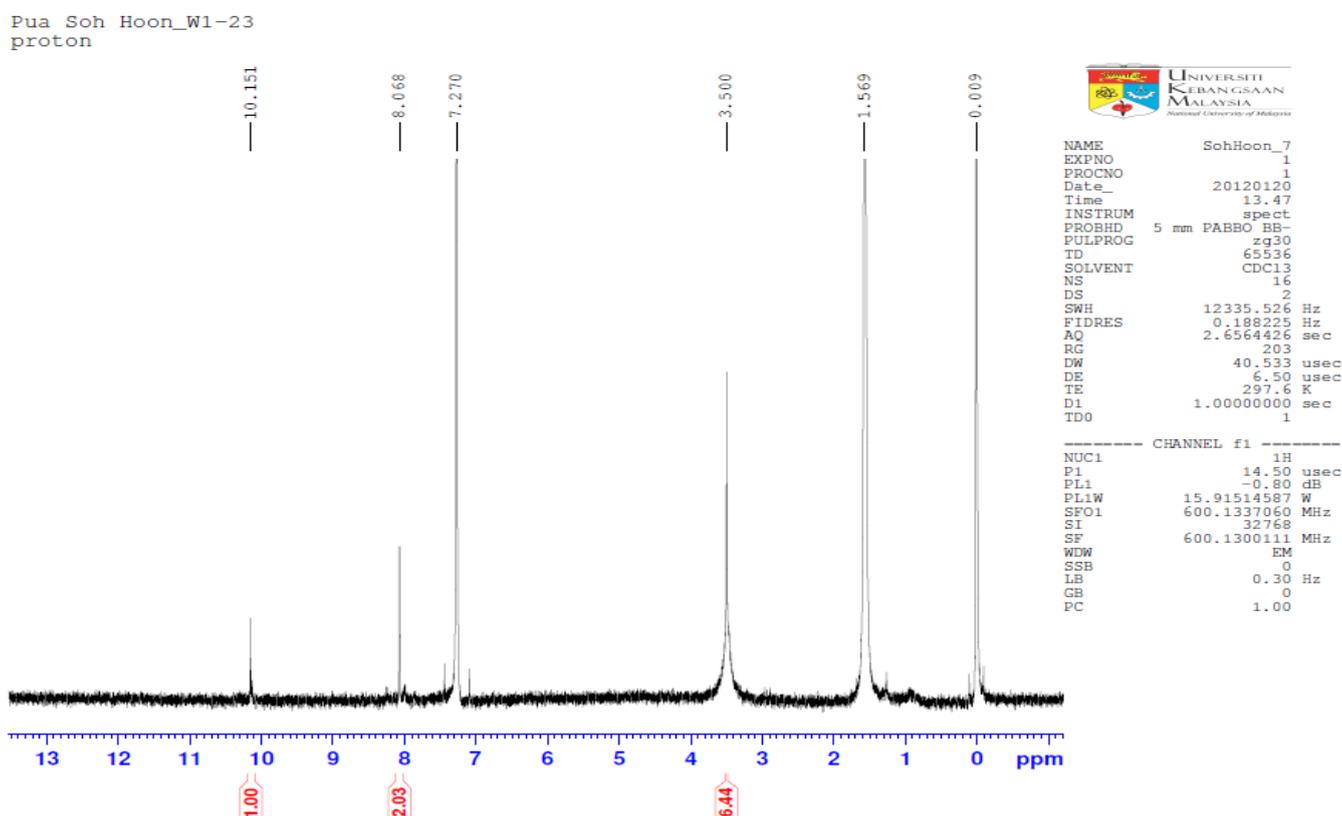
2.2. Electrochemical Measurements

Open Circuit Potential (OCP)

Changes in the OCP values in the presence of an inhibitor are often useful indicators of which reactions are more affected, *i.e.*, cathodic or anodic. The OCP of mild steel was monitored at different temperatures in the absence and presence of 0.5 mM PBB. Figure 3 presents the effect of the absence and presence of the PBB inhibitor on the variation of the OCP of mild steel at different temperature in 1.0 M HCl solution. It is obvious from Figure 3 that the addition of PBB to the HCl solutions shifts the

OCP of the mild steel to more positive values at all of the studied temperature. This positive shift of the OCP in the presence of PBB indicates that PBB has influenced the anodic reaction of mild steel corrosion. The maximum shift in OCP was 54 mV at 30 °C. This preliminary result suggests that PBB can retard the anodic reactions under open circuit conditions: the oxidation on the surface of mild steel [15,16]. In both presence and absence of PBB, the OCP values are shifted towards the positive direction with increasing temperature, reflecting the deterioration of the surface layers for the inhibitor and for the oxide, respectively.

Figure 3. The change in OCP as a function of temperature for mild steel in 1.0 M HCl in the absence and presence of 0.5 mM PBB.
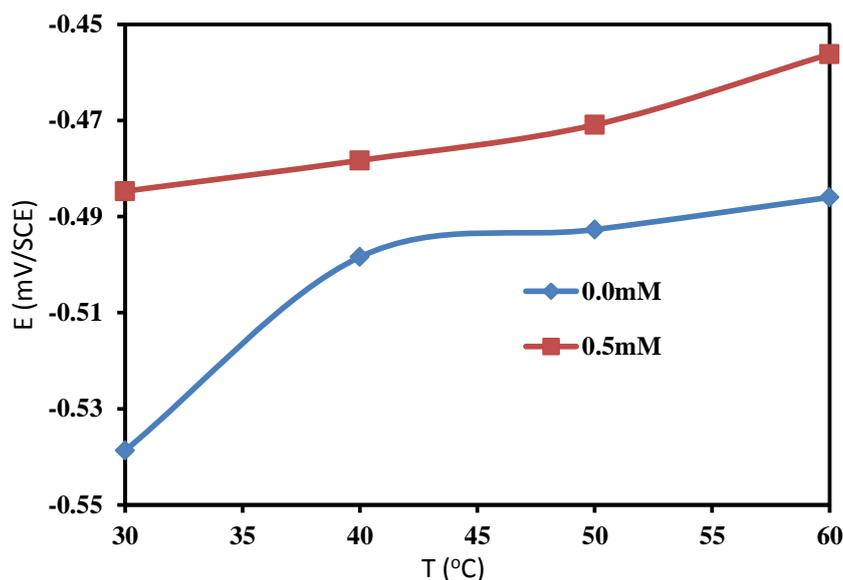
2.3. Polarisation Measurements

The numerical values of the variations in corrosion current density (i_{corr}), corrosion potential (E_{corr}), anodic Tafel slope (β_a), cathodic Tafel slope (β_c) and inhibition efficiency (*IE%*) with the concentrations of inhibitor PBB at all studied temperatures are depicted in Table 1. The *IE%* is calculated as [17]:

$$IE\% = \frac{i_{corr(uninh)} - i_{corr(inh)}}{i_{corr(uninh)}} \times 100 \tag{1}$$

where $i_{corr(uninh)}$ and $i_{corr(inh)}$ are the corrosion current densities in the absence and presence of inhibitor, respectively. Close examination of Table 1 shows that an increase in temperature increases i_{corr}, while the addition of PBB decreases the i_{corr} values across the temperature range. The results also indicate that the inhibition efficiencies increased with the concentration of inhibitor but decreased proportionally with temperature. Such behavior can be interpreted on the basis that the inhibitor acts by adsorbing onto the metal surface, and an increase in temperature results in desorption of some adsorbed inhibitor molecules, leading to a decrease in the inhibition efficiency [18]. In acidic solutions, the anodic reaction of corrosion is the passage of metal ions from the metal surface into the solution, and the cathodic reaction is the discharge of hydrogen ions to produce hydrogen gas or to reduce

oxygen. The inhibitor may affect either the anodic or the cathodic reaction, or both [19]. Since the β_a and β_c of PBB were found to change with inhibitor concentration, this indicates that the inhibitor affected both of these reactions, however it's more dominated on the anodic reaction based on the OCP results.

Table 1. Polarisation parameters for mild steel in 1.0 M HCl with various concentrations of PBB at different temperatures.

Temperature ℃	Concentration mM	β_a V·dec^{-1}	$-\beta_c$ V·dec^{-1}	i_{corr} µA·cm^{-2}	$-E_{corr}$ mV *vs.* SCE	*IE%*
30	0.0	0.127	0.119	461.0	525	–
30	0.1	0.078	0.104	146.0	480	68.34
30	0.2	0.064	0.090	43.8	510	90.05
30	0.3	0.076	0.091	35.2	471	92.36
30	0.4	0.085	0.095	34.3	470	92.56
30	0.5	0.058	0.086	22.5	461	95.12
40	0.0	0.188	0.145	1950	481	–
40	0.5	0.064	0.090	196.1	466	89.94
50	0.0	0.226	0.168	4320	477	–
50	0.5	0.071	0.100	604.8	480	86.00
60	0.0	0.354	0.241	14000	486	–
60	0.5	0.094	0.125	2520	487	82.00

The addition of PBB inhibitor shifts the E_{corr} values towards the positive; this follows the OCP trend. A compound can be classified as an anodic- or a cathodic-type inhibitor when the change in the E_{corr} value is larger than 85 mV [20]. Since the largest displacement exhibited by PBB was 40 mV at 30 ℃ (Table 1), it may be concluded that this molecule should be considered as a mixed-type inhibitor. The polarization profile of mild steel in 1.0 M hydrochloric acid at 30 ℃ in the presence and absence of PBB is shown in Figure 4. The presence of increasing amounts of PBB led to a decrease in both the cathodic and anodic current density.

Figure 4. Potentiodynamic polarization curves for mild steel in 1.0 M HCl at 30 ℃ containing various concentration of PBB.
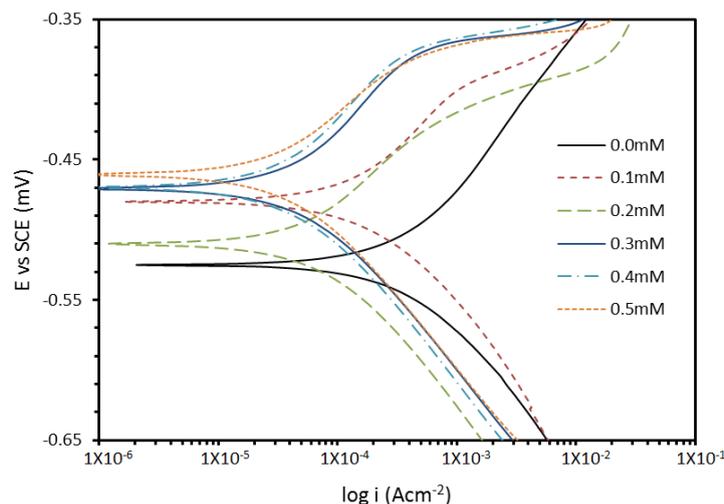
Adsorption is the mechanism generally accepted to explain the inhibitory action of organic corrosion inhibitors. The adsorption of inhibitors can affect the corrosion rate in two ways: (i) by decreasing the available reaction area, the so called geometric blocking effect and (ii) by modifying the activation energy of the cathodic and/or anodic reactions occurring in the inhibitor free metal in the course of the inhibited corrosion process. It is a difficult task to determine which aspects of the inhibiting effect are connected to the geometric blocking action and which are connected to the energy effect. Theoretically, no shifts in E_{corr} should be observed after addition of the corrosion inhibitor if the geometric blocking effect is stronger than the energy effect [18]. The change observed in the OCP and E_{corr} values upon addition of PBB indicates that the energy effect is stronger, although the blocking effect cannot be ignored.

2.4. Electrochemical Impedance Spectroscopy (EIS) Measurements

The experimental results obtained from EIS measurements of the corrosion of mild steel in the presence and absence of inhibitor at 30, 40, 50 and 60 ℃ are summarized in Table 2.

Table 2. Impedance data for mild steel in 1.0 M HCl for various PBB concentrations at different temperatures.

Temperature ℃	Conc. mM	R_{ct} ohm·cm^2	R_s ohm·cm^2	C_{dl} µF·cm^{-2}	*IE%*
30	0.0	46.89	1.715	512.0	–
30	0.1	234.6	1.867	379.8	80.00
30	0.2	268.9	1.567	182.9	82.56
30	0.3	313.4	1.672	182.3	85.04
30	0.4	338.7	1.644	155.1	86.16
30	0.5	378.1	1.608	145.2	87.60
40	0.0	13.22	1.127	1226	–
40	0.5	88.13	2.122	307.7	85.00
50	0.0	7.02	1.014	1284	–
50	0.5	31.02	1.310	326.9	77.37
60	0.0	3.03	1.067	1371	–
60	0.5	8.67	1.696	691.1	65.04

The impedance spectra for mild steel in 1.0 M HCl with and without various concentrations of PBB at 30 ℃ are presented as Nyquist plots in Figure 5.

A considerable increase in the total impedance was recorded with the addition of PBB. It can be concluded from Figure 5 that the impedance response of mild steel significantly changed after the addition of PBB in the corrosive solution. This can be attributed to an increase in substrate impedance with the increase in inhibitor concentrations. In the impedance spectra of mild steel in the absence and presence of PBB, the Nyquist plots consist of one semi-circle which attributed to the charge-transfer process. Similar behavior was noted for all of the studied temperatures. Randles equivalent circuit which consists of solution resistance (R_S) in series with the parallel combination of the double-layer capacitance (C_{dl}) and a charge-transfer resistance (R_{ct}) was used to fit the EIS data.

Figure 5. Nyquist plot for mild steel in 1.0 M HCl at 30 °C containing various concentration of PBB.
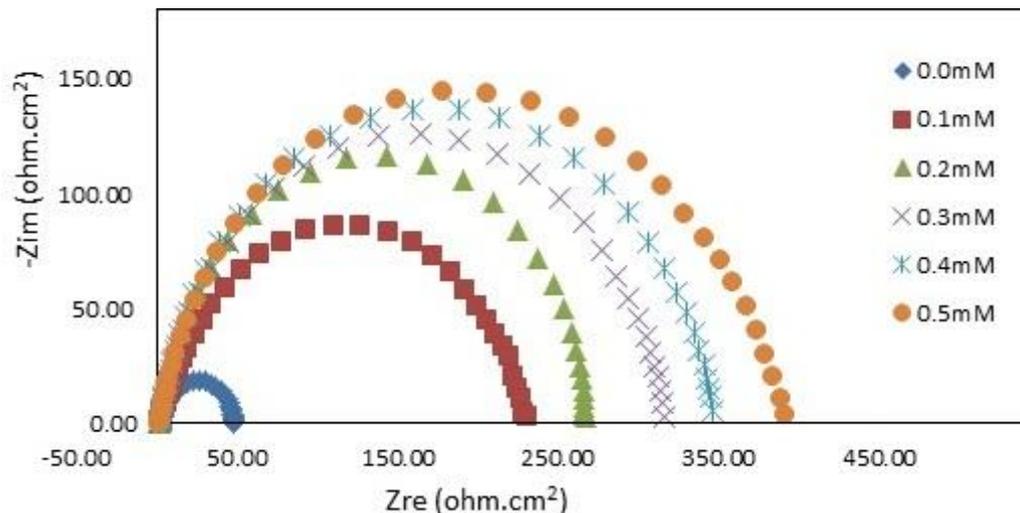
$$IE\% = \frac{R_{ct(inh)} - R_{ct(uninh)}}{R_{ct(inh)}} \times 100 \qquad (2)$$

In this equation, $R_{ct(inh)}$ and $R_{ct(uninh)}$ are the charge transfer resistance with and without the PBB inhibitor, respectively. Table 2 indicates that the R_{ct} increased and C_{dl} decreased with increasing PBB concentration. A large charge-transfer resistance is associated with a slowly corroding system [21]. In addition, improved inhibitor protection is associated with a decrease in the metal capacitance. The decrease in C_{dl}, which resulted from a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that PBB acted via adsorption at the metal/solution interface [22]. The corrosion reaction decreased the homogeneity of the adsorbed PBB film. This was confirmed by the fact that the C_{dl} values increased over the temperature range. *IE*% increased as the inhibitor concentration increased, but decreased proportionally with temperature. This result follows the same general trend of the *IE*% obtained from the potentiodynamic polarization.

Postulated Inhibition Mechanism

Generally organic inhibitors are adsorbed on the metal surface and prevent further dissolution of metal through blocking of either the cathodic or anodic reaction or both. Organic inhibitors, capable of forming insoluble complexes, or chelates, with metallic ions present on the surface of metal. The inhibition efficiency of our corrosion inhibitor against the corrosion of steel in 1M HCl can be explained on the basis of the number of adsorption sites, their charge density, molecular size, mode of interaction with the metal surface and the ability to form metallic complex. The π electrons and free electrons on the S and N atoms form bonds with the metal surface Figure 6.

Figure 6. The postulated mechanism of PBB as corrosion inhibitor.
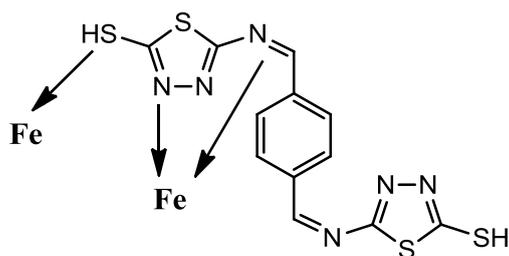
The PBB can be easily protonated in the hydrochloric acid solution because the molecule is made of a planer of 1,3,4-thioziazle ring, and also contains S, and N atoms with lone pair electrons and π electrons. Coordinate covalent bond formation between electron pairs of un protonated S atom and N atoms with metal surface can take place. In addition, PBB molecules are chemically adsorbed due to the interaction of π-orbitals with metal surface. The inhibitor is very stable organic molecule it has made of a planer of 1,3,4-thioziazle ring and benzene rig in addition of double bond of azomethine group. The resonance structures of PBB give the molecule more stability Scheme 2.

Scheme 2. The PBB tautomerism.
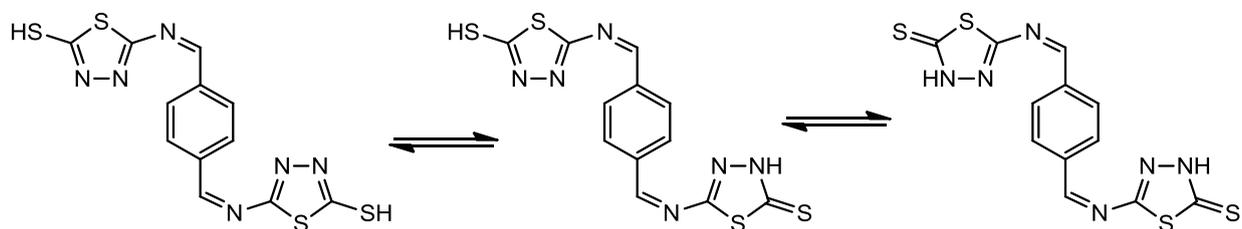
The inhibiting performance exhibited by the PBB may be due to the presence of protonated form of nitrogen and sulphur atoms of the PBB which makes it adsorb quickly on the mild steel surface, thus forming an insoluble stable film on the surface of the mild steel. In the present study, the value of Total Energy is 34.7675 kcal/mol, hence, showing that adsorption of PBB molecule on the surface of mild steel takes place through both physical as well as chemical processes Figure 7.

Figure 7. Three dimensional structure of PBB.
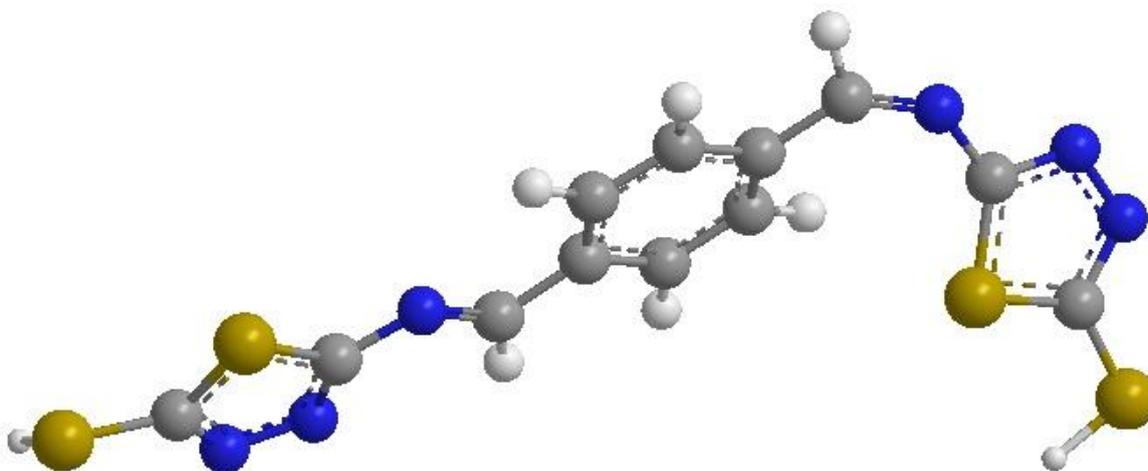
3. Experimental Section

3.1. Synthesis of Corrosion Inhibitor PBB

All chemicals used were of reagent grade (supplied by Sigma-Aldrich, Selangor, Malaysia) and used as supplied without further purifications. A solution of the 5-amino-2-mercapto-1,3,4-thiadiazole (0.4 mmol) in ethanol 25 mL was refluxed with terephthalaldehyde 0.2 mmol) for 20 h. After cooling to room temperature, a solid mass separated and recrystallized. Recrystallized from ethanol; yield 85%; ^{1}H-NMR (CDCl$_3$): δ 8.068, (s, 2H, N=CH), δ 7.270 (s, 4H, C–H aromatic ring) and δ 3.500 (s, 2H) for S–H; IR: 3100.0 cm^{-1} (C–H, aromatic), 1694.7 cm^{-1} (C=N, imine), 1608.5 cm^{-1} (C=N, imine), 1660.0 cm^{-1} (C=C, aromatic); Elemental Analysis: C, Anal. Calcd. for C$_{12}$H$_8$N$_6$S$_4$: C, 39.54%; H, 2.21%; N, 23.06%. Found: C, 38. 69%; H, 2.87%; N, 22.70%. The FTIR spectra were measured using Thermo Scientific Model Nicolate 6700 Spectrophotometer (Thermo Scientific, Hemel Hempstead, UK). NMR spectra were recorded using Model AVANCE III 600 MHz spectrometer (BRUKER, Billerica, MA, USA).

3.2. Electrochemical Measurements

Mild steel specimens obtained from the Metal Samples Company were used as the working electrodes throughout the study. The composition (wt%) of the mild steel was: Fe, 99.21; C, 0.21; Si, 0.38; P, 0.09; S, 0.05; Al, 0.01. The specimens were cleaned according to ASTM standard G1-03 [23]. Measurements were carried out in aerated non stirred 1.0 M HCl solutions at 30, 40, 50 and 60 ℃ with a PBB concentration range of 0.1–0.5 mM as a corrosion inhibitor. Electrochemical measurements were conducted with Gamry water-jacketed glass cell (Gamry Instruments, Warminster, PA, USA). The cell contained three electrodes, the working, counter and reference electrodes, comprised of mild steel, a graphite bar and a calomel electrode (SCE), respectively. Measurements were performed using a Gamry Instrument Potentiostat/Galvanostat/ZRA model Ref 600. DC105 and EIS300 software by Gamry were used for potentiadynamic scans and electrochemical impedance spectroscopy (EIS). The potentiodynamic current-potential curves were swept from −0.25 to +0.25 VSCE at a scan rate of 0.5 mV·s^{-1}. Impedance measurements were carried out using AC signals of 5mV peak to peak amplitude at the open circuit potential in the frequency range 0.1–100 Hz. All impedance date were fitted to appropriate equivalent circuits (EC) using Gamry Echem Analyst software. Experiments for electrochemical measurements were initiated about 30 min after the working electrode was immersed in the solution to stabilise the steady state potential. All measurements were performed in triplicate, and average values are reported.

4. Conclusions

5,5'-((1Z,1'Z)-(1,4-phenylenebis(methanylylidene))bis(azanylylidene))bis(1,3,4-thiadiazole-2-thiol) (PBB), was successfully synthesized and characterized using various spectroscopic methods. Electrochemical measurments such as open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization were used to study the corrosion inhibition of mild steel in 1.0 M HCl solutions at different temperature, using PBB as an inhibitor. This compound

exhibited excellent inhibition performance as a mixed-type inhibitor. In general, the acidic corrosion of mild steel was reduced upon the addition of an appropriate concentration of PBB. The inhibition efficiencies were increased with inhibitor concentration but decreased with solution temperature.

Acknowledgements

Conflicts of Interest

The authors declare no conflict of interest.

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