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Research paper

Newly Synthesized *N*-Substituted Thiosemicarbazone as a Potential Corrosion Inhibitor for Mild Steel in 1 M HCl

N. Z. Nor Hashim[1*], K. Kassim[2], F. H. Zaidon[3]

[1]Faculty of Applied Sciences, Universiti Teknologi MARA, Perak Branches, Tapah Campus, Tapah Road, 35400 Perak, Malaysia
[2]Centre of Nanomaterials, Institute of Science, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
[3]Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
**Corresponding author E-mail: norzakiah@perak.uitm.edu.my*

Abstract

Two *N*-substituted thiosemicarbazone derivatives namely as 2-(4-chlorobenzylidene)-*N*-phenylhydrazinecarbothioamide and 2-benzylidene-*N*-phenylhydrazinecarbothioamide (L1 and L2, respectively) have been tested as corrosion inhibitors on mild steel in 1 M HCl. The ligands were synthesized and investigated using potentiodynamic polarization (PD) and electrochemical impedance spectroscopy (EIS). The obtained results indicated that inhibition efficiency, (IE, %) L1 increased with increasing inhibitor concentrations which behaved as a good corrosion inhibitor compared to L2. The synthesized ligands were successfully characterized by melting point, elemental analysis (C, H, N, and S), Fourier-transform infrared spectroscopy (FT-IR) and NMR (^{1}H and ^{13}C) spectroscopy. The excellent inhibition effectiveness for both compounds on mild steel before and after immersion in 1 M HCl solution containing 40 ppm of L1 and L2 were also verified by scanning electron microscope (SEM). Based on potentiodynamic polarization results, it can be concluded that all investigated compounds are mixed-type inhibitors and obey the Langmuir adsorption isotherm.

Keywords: *Thiosemicarbazone, corrosion inhibitor, mild steel, 1 M HCl*

1. Introduction

The application of corrosion inhibitors on mild steel in acidic media is important for some industrial facilities (Herle et al., 2011). Acid solutions especially hydrochloric acid is generally used for the removal of rust and scale in industrial processes (Kadhum et al., 2014). The acid solutions may cause metal corrosion leading to a big loss amount in profit for related industries. Hence, corrosion inhibitors were introduced to protect the mild steel. Most of the effective corrosion inhibitors are the organic compounds containing nitrogen, oxygen, sulfur, aromatic rings and π-electron in their structures (Nahlé et al., 2012). Thiosemicarbazone has been investigated widely as good corrosion inhibitors for mild steel in acidic medium (Jacob & Parameswaran, 2010; Goulart et al., 2013). Due to the presence of nitrogen and sulfur atoms in the structures, thiosemicarbazone inhibitors show as an effective corrosion inhibition efficiencies (Bisceglie et al., 2015). This work aimed to synthesize, characterize and investigate the inhibiting properties of L1 and L2 on the corrosion of mild steel in 1 M HCl through electrochemical techniques like linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS).

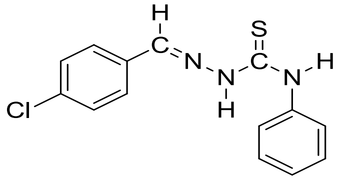
2. Experimental

2.1 Synthesis of ligands

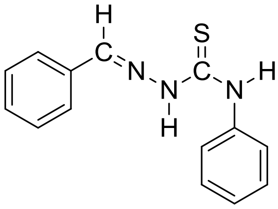
Figure 1 shows the molecular structures and IUPAC names of inhibitors, L1 and L2, which is used as mild steel corrosion inhibitors. The synthesis method was adopted from Abdalla and his co-workers, 2015. A mixture of 4-chlorobenzaldehyde (5 mmol) and benzaldehyde (5 mmol) with 4-phenylthiosemicarbazide (5 mmol) was refluxed in 25 mL of absolute ethanol for 3 hours to synthesize L1 and L2, respectively. Then, a few drops of concentrated of sulfuric acid were added in the mixtures to adjust the pH. The obtained precipitation was separated by filtration, washed with ethanol and dried over silica gel. The ligands were characterized using CHNS, FTIR, ^{1}H and ^{13}C NMR and were compared with the data by (Hernándeza et al., 2008):

For L1: Color: Yellow. Yield: 95.76%. Melting Point: 203-205℃. Elemental Analysis. Calc. for $C_{14}H_{12}ClN_3S$: C, 58.03; H, 4.17; N, 14.50; S, 11.07. Found: C, 55.38; H, 4.01; N, 11.71; S, 14.61%. Molecular weight: 289.78. Main IR peaks (KBr, cm-1): ν(N-H) 3310s, 3138w; ν(C=N) 1596s; ν(C=S) 815m. ^{1}H NMR ($CDCl_3$, ppm): 10.26 (s,1H, N(2)H); 9.18 (s,1H, N(3)H), 7.95 (s,1H,C=N(1)); 7.68-7.28 (m,9H, Ar-H); ^{13}C NMR ($CDCl_3$, ppm): 175.91 (C=S); 159.99 (C=N); 125.49-143.84 (Ar-H).

For L2: Color: White. Yield: 72.10%. Melting Point: 190-192℃. Elemental Analysis. Calc. for $C_{14}H_{13}N_3S$: C, 65.85; H, 5.13; N, 16.46; S, 12.56. Found: C, 62.74; H, 5.10; N, 17.85; S, 12.09%. Molecular weight: 255.34. Main IR peaks (KBr, cm-1): ν(N-H) 3304w, 3160s; ν(C=N) 1570s; ν(C=S) 858m. ^{1}H NMR ($CDCl_3$, ppm): 10.32 (s,1H, N(2)H); 9.20 (s,1H, N(3)H), 8.01 (s,1H, HC=N(1)); 7.36-7.87 (m,9H, Ar-H); ^{13}C NMR ($CDCl_3$, ppm): 175.88 (C=S); 143.30 (C=N); 124.80-137.84 (Ar-H).



2-(4-chlorobenzylidene)-*N*-phenylhydrazinecarbothioamide, (L1)



2-benzylidene-*N*-phenylhydrazinecarbothioamide, (L2)

Figure 1: Molecular structure of compound L1 and L2 and their IUPAC names

2.2. Materials and solutions

A mild steel (Q-Panel) sample with dimensions about 2 cm x 1 cm x 0.025 cm was embedded in epoxy resin, exposing 0.049 cm^2 surface area to the electrolyte. The electrode surface was polished with different grades of emery papers, i.e, 800 and 1200 grade and finally rinsed with distilled water. The acidic solution of 1 M HCl was prepared by dilution of 37% HCl from R&M Chemicals with ultra-pure water. Next, different concentrations of 10, 20, 30, and 40 ppm of inhibitors were dissolved in 5 mL of ethanol to solve the solubility problems. Then, each concentration solutions were diluted with 1 M HCl solution in 100 mL of volumetric flask.

2.3. Electrochemical Measurements

A three-electrode cell consisting of mild steel as a working electrode, a platinum rod as a counter electrode and a silver/silver chloride (Ag/AgCl, 3.0 M KCl) was used as reference electrode. The experiments were carried out using an Auto-lab PGSTAT-302N potentiostat/galvanostat. The polarization measurements were performed using a scan rate of 1 mV/s in the potential range of ±250 mV around the open circuit potential (E_{ocp}). The corrosion current density (I_{corr}) values were obtained using Tafel extrapolation method and the inhibition efficiency (IE, %) was calculated according to the equation (1) (Xu et al., 2013):

$$IE,\% = \frac{I_{corr'} - I_{corr}}{I_{corr}} \text{ x } 100 \qquad (1)$$

where the $I_{corr'}$ and I_{corr} are the corrosion current density without and with inhibitors, respectively.

The EIS measurements were carried out in a frequency range of 100 kHz to 0.1 Hz in a combination of the peak-to-peak amplitude of 0.1 to 0.01 Hz. The impedance data were analyzed with FRA software. Polarization resistance (R_p) and constant phase element (CPE) were obtained from Nyquist plots. The (IE, %) values were calculated from the R_p values according to equation (2) (John et al, 2017):

$$IE,\% = \frac{\mathbf{R_p} - \mathbf{R}_{p'}}{\mathbf{R_p}} \text{ x } 100 \qquad (2)$$

where R_p and $R_{p'}$ are the polarization resistance of inhibited and uninhibited solutions, respectively.

2.4. SEM experiments

A Hitachi SEM TM 3030 Plus was used to observe the surface morphology of mild steel samples before and after 24 hours' immersion in 1 M HCl solution in the absence and presence of the inhibitors.

3. Results and Discussion

3.1. Polarization Measurements

Figure 2a and b show Tafel polarization plots of mild steel in 1 M HCl without and with different concentrations of thiosemicarbazone compounds. In Figure 2, both anodic and cathodic current densities decrease as the inhibitor concentrations increased. This is due to the adsorption of the inhibitors on the mild steel surface which reduces both anodic dissolution of iron at anodic sites and cathodic evolution of hydrogen at cathodic sites (Shahabi & Reza, 2015). The parameters including the corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (β_c and β_a), and the corrosion density (I_{corr}) are listed in Table 1. From Table 1, the E_{corr} values having a displacement at around 69 mV away from the blank solution in the cathodic direction. Thus, the general results indicate that each investigated inhibitors are mixed-type with cathodic character predominating, hence able to retard both of the anodic and cathodic reactions of mild steel in the 1 M HCl. If the difference in E_{corr} values found to be exceeding $\mp$85 mV in inhibited solution either in cathodic or anodic direction with respect to the blank solution, that particular inhibitor is known as cathodic or anodic type inhibitor.

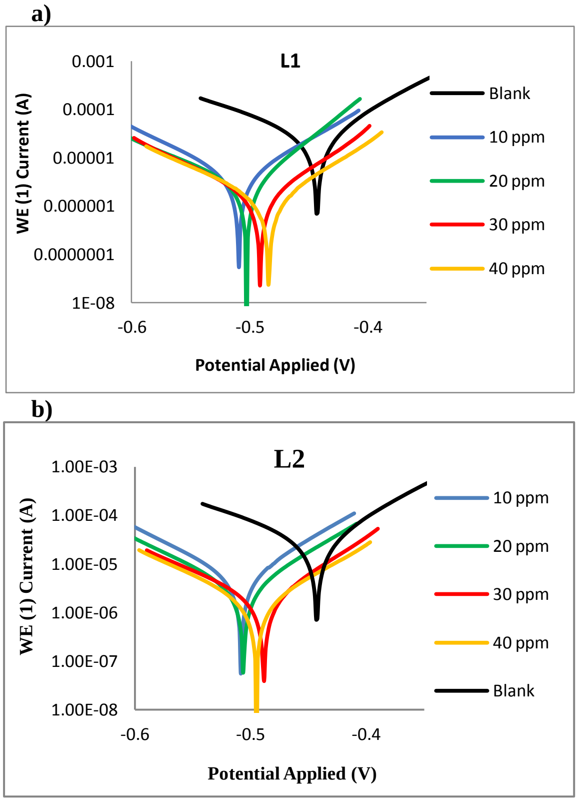


Figure 2: Polarization curves of mild steel in 1 M HCl solution without and with different concentrations of a) L1 and b) L2

Table 1: Polarization parameters for mild steel in 1 M HCl solution in the absence and presence of various concentrations of L1 and L2

Inhibitors	Conc. (ppm)	i_{corr} (μA/cm^2)	-E_{corr} (mV)	βc (mV/dec)	βa (mV/dec)	IE (%)
Blank	-	569.48	442.61	77.50	123.65	-
L1	10	97.49	508.09	82.34	96.18	82.88
	20	58.45	500.68	56.42	105.83	89.74
	30	37.77	490.12	74.54	99.60	93.37
	40	32.18	482.70	78.20	103.91	94.35
L2	10	112.76	508.01	75.37	92.07	80.20
	20	70.68	505.13	77.01	96.70	87.59
	30	42.09	486.94	73.67	107.68	92.61

	40	37.29	494.12	89.37	101.74	93.45

40	278.08	1.98	87.94

3.2. EIS Measurements

Nyquist plots of mild steel in 1 M HCl in the absence and presence of inhibitors with different concentrations are represented in Figure 4a and b, respectively. From Figure 4, the diameter of the semicircles increases with increasing the inhibitors concentration. These results suggested that the inhibition efficiency increases by increasing inhibitor concentrations. The IE, % values were calculated using equation (2). The parameters namely, the polarization resistance (R_p) and constant-phase element (CPE) were calculated from the plot are listed in Table 2. The polarization resistance (R_p) values increases and constant-phase element (CPE) decreases with the increasing of inhibitor concentrations. This indicates that the addition of the inhibitors had retarded the corrosion reactions on the mild steel surface by the formation of an inhibitive layer. Moreover, the coverage of the mild steel surface by the film decreases the double layer thickness (Khaled et al., 2010). Based on the observations, the impedance data for both compounds and concentrations showed a similar trend to that of the polarization measurement. It was concluded that the order of IE, % based on EIS measurements for the inhibitors is L1 > L2.

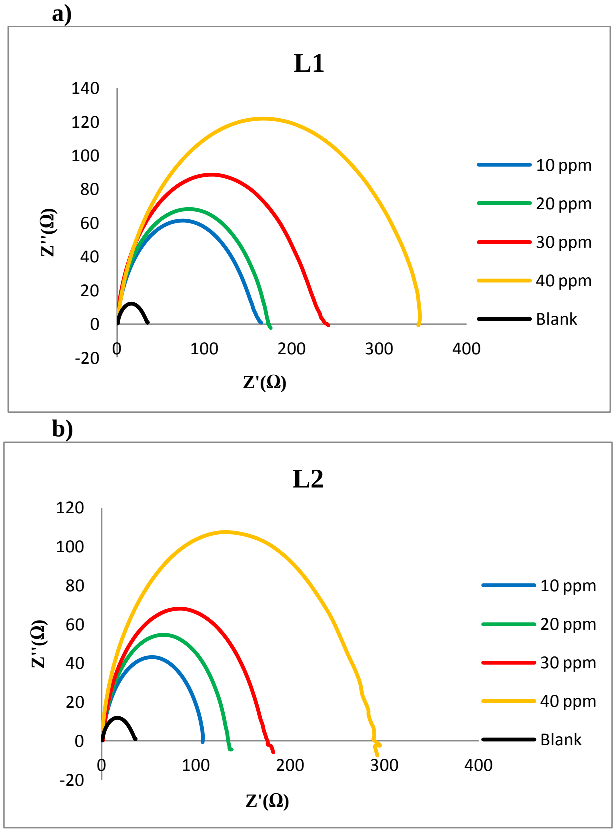


Figure 3: Nyquist impedance plots of mild steel in 1 M HCl solution in the presence of various concentrations of a) L1and b) L2

Table 2: Electrochemical impedance parameters for mild steel in 1 M HCl solution in the absence and presence of various concentrations of L1 and L2

Inhibitors	Conc. (ppm)	R_p (Ω cm^2)	CPE (μF cm^{-2})	IE (%)
Blank	-	33.53	8.44	-
L1	10	156.32	4.30	78.55
	20	168.91	3.57	80.15
	30	224.80	2.62	85.08
	40	338.13	2.37	90.08
L2	10	106.96	4.42	68.65
	20	132.42	3.85	74.68
	30	169.69	3.49	80.24

3.3. SEM studies

The surface morphology of mild steel samples was examined by SEM after immersion in 1 M HCl with and without of 40 ppm inhibitors for 24 hours as shown in Figure 4. Figure 4a shows the mild steel surface which has been immersed in 1 M HCl solution in the absence of inhibitors whereas Figure 4b and c represents the SEM images of mild steel surface after immersion in an acidic solution containing 40 ppm of inhibitors L1 and L2, respectively. The results proved that inhibitor can be adsorbed on the mild steel surface and protect the surface from hydrochloric acid solution (Liu et al., 2015).

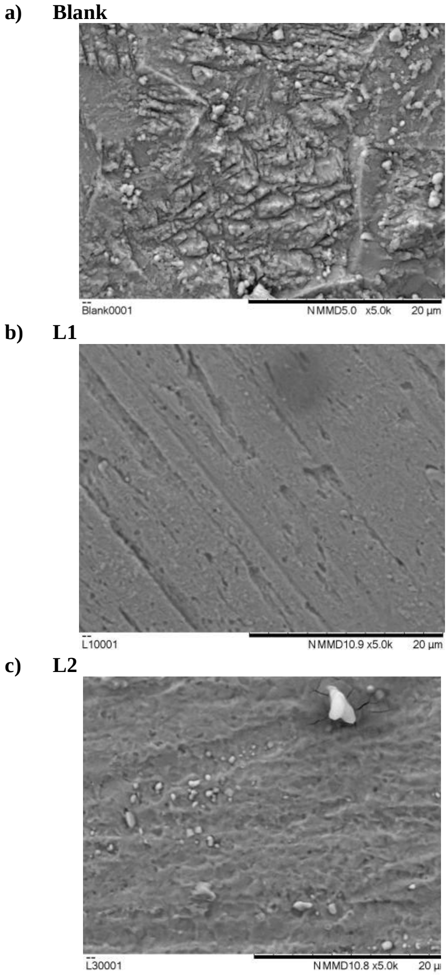


Figure 4: SEM images of mild steel in 1 M HCl solution after 24 hours of immersion a) without inhibitors, b) with inhibitors 40 ppm of L1 and c) with inhibitors 40 ppm of L2

3.4. Adsorption isotherm

Adsorption isotherms are very important in order to gain information about the mechanism of organic electrochemical reactions. The most frequently used adsorption isotherms are Langmuir, Temkin, and Frumkin. In this study, Langmuir adsorption isotherm has been tested and it is found that all compounds obey the isotherm. The plot of C/θ vs. C yields straight lines with slopes almost equal unity (R^2 is between 0.9962 and 0.9985) as shown in Figure 5. The Langmuir isotherm is defined according to the equation (3) (Leçe et al., 2008):

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (3)$$

where θ denotes the surface coverage, C_{inh} is the inhibitor concentration and K_{ads} is the adsorption equilibrium constant.

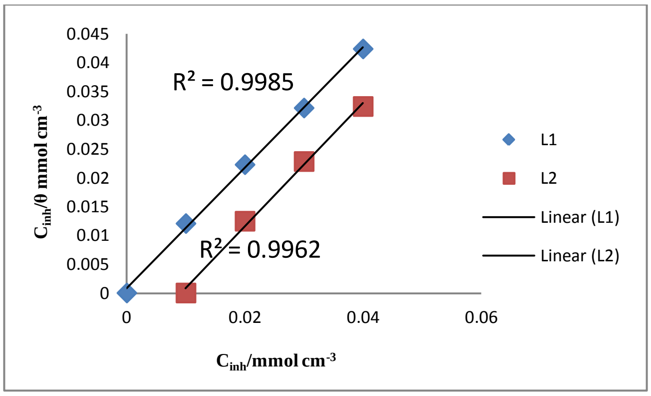


Figure 5: Langmuir plots for L1 and L2 on mild steel in 1 M HCl solution

3.5. Effect of substituents

Analysis of the effects of substituents indicated that chloride substitution (L1) achieved a better inhibition than that of no substitution (L2) at all concentrations under study. This is influenced by the nature and charges of the metal surface, the chemical structure of the organic inhibitor, the type and number of bonding atoms or groups in the molecule and the type of electrolyte solutions. L1 is an electron donating groups (EDG) which containing chloride substituents that activate the aromatic ring where the π-electrons are pushed towards the ring and the electron density of the aromatic ring increase. This is due to the resonance effects. Thus, the aromatic ring of L1 become a good donor and it enriches the electron density at the azomethine group (C=N). Due to this reason is why L1 reveals as a more effective inhibitor compared to L2.

4. Conclusion

The inhibiting action of thiosemicarbazone derivatives, (L1 and L2) on the corrosion of mild steel in 1 M HCl solution has been studied using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques and their inhibition efficiency follows the order: L1 > L2. Inhibition efficiency increased with increasing of inhibitor concentrations. Both inhibitors are mixed-type and adsorbed on mild steel surface to block its active sites. SEM analysis shows that the inhibitor molecules form a protective film on the mild steel surface in 1 M HCl solution and obey Langmuir adsorption isotherm.

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