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Synthesis and Corrosion Inhibition Studies of *N*-((4 and 3-chlorophenyl) carbamothioyl) Benzamide in 1M H_2SO_4

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ABSTRACT

In this study, the new compound of thiourea derivatives were successfully synthesized, namely *N*-((3-chlorophenyl) carbamothioyl) benzamide (T1) and *N*-((4-chlorophenyl) carbamothioyl) benzamide (T2). These series of thiourea compounds were prepared from the reaction of benzoyl chloride with ammonium thiocyanate to produce benzoyl isothiocyanate, then direct reaction with amines by using condensation method. Their structures were characterized on the basis elemental analysis and spectroscopic techniques namely infrared and nuclear magnetic resonance. The Infrared spectra showed the significant results of stretching vibrations of the compounds are v(C=O), v(C=S) and v(C-N) at 1533.39-1671.00 cm^{-1}, 1256.64-1261.73 cm^{-1} and 1144.22-1144.81 cm^{-1}, respectively. These compounds were investigated as corrosion inhibitors on mild steel in 1M H_2SO_4 using linear polarization techniques. Results show the highest inhibition efficiency of T1 is 55% while for T2 is 73%. The percentage inhibition efficiency of T2 is higher than T1 due to the difference position of substituent at *meta* and *para*.

Keywords: Corrosion inhibition, linear polarization, mild steel, thiourea

INTRODUCTION

Corrosion is an event that occurs naturally in our environment. From previous studies, some of inhibitors can be added to the acid media to reduce the rate of corrosion to safe level (Shetty & Shetty, 2008). The inhibitor molecules get bonded to the surface of mild steel by chemisorption, physisorption, or complexation with the polar groups acting as the reactive centres in the molecules (Sundaram & Sundaravadivelu, 2016). The

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good acid inhibitors used in the industry are compounds having multiple bonds in their molecules, mainly contain nitrogen and sulphur atoms through which are capable of retarding metallic corrosion and easily adsorbed on the metal surface (Shetty, Shetty, & Nayak, 2008). Thiourea is an organosulphur compound which has a group of nitrogen, carbon, hydrogen and sulphur. It is generally identical as urea except the position of oxygen replaced with sulphur atom. Thiourea and its derivatives appear as white, lustrous crystal or flaky solids and very useful in pharmaceuticals (Miftah & Tjahjono, 2015). The chemical structure of thiourea is $(NH_2)_2CS$ while urea is $(NH_2)_2CO$. Some substituted thiourea derivatives have been studied in considerable detail as effective corrosion inhibitors for mild steel in acidic media (Yadav, Al-Majidi, & Al-Saadie, 2014). The presence of both hard and soft donor atoms in the ligand increases the coordination ability towards a metal centre (Yusoh, Jusoh, Khairul, & Yamin, 2010).

In a continuation of our research, we reported the synthesis of thiourea compounds, namely, N-((3-chlorophenyl) carbamothioyl) benzamide) [T1] and N-((4-chlorophenyl) carbamothioyl) benzamide) [T2] as shown in Figure 1. For all the compounds, the only difference was the position of chloride group at *meta* and *para* position. The structures of the ligands have been characterized by elemental analysis (CHNS), IR spectroscopy, ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) and melting point. The compounds were undergoing corrosion inhibition using linear polarization techniques.

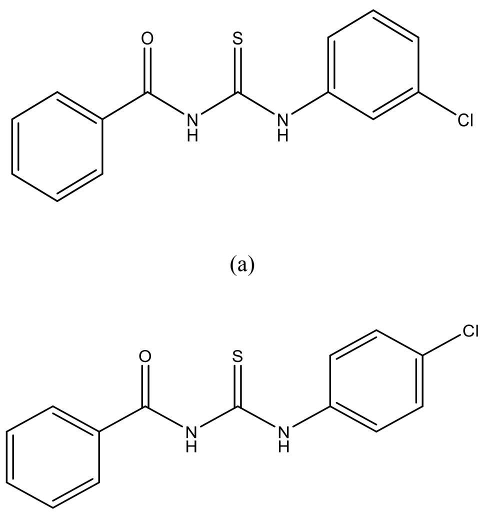


Figure 1. The chemical structure of the investigated compounds: (a) *N*-((3-chlorophenyl) carbamothioyl) benzamide (T1); and and (b) *N*-((4-chlorophenyl) carbamothioyl) benzamide (T2)

MATERIALS AND METHOD

Synthesis of Thiourea Derivatives

The benzoylthiourea ligands were prepared according to the previous study with a slight modification (Al-jeilawi, Al-Majidi, & Al-Saadie, 2013). The purity of ligands was tested by using Nuclear Magnetic Resonance (NMR), Infrared Spectroscopy (IR) and Elemental Analysis (CHNS). The melting point, percentage yield, CHNS, IR and NMR data of the synthesized compounds were shown in Figure 2.

Specimen Preparation

The steel coupons were even and smooth. After polishing, the specimens were washed with distilled water and acetone before being dried and stored in desiccator (Edrah & Hasan, 2010).

Preparation of N-((3-chlorophenyl) carbamothioyl) benzamide [T1]

The ammonium thiocyanate (0.01 mol, 0.761 g) was diluted into 20 ml of acetone to form a solution. Then, (0.01 mol, 1.162 ml) of benzoyl chloride was added into the mixture and stirred for 20 minutes. The 3-chloroaniline (0.01 mol, 1.058 ml) was mixed with 5 ml of acetone to form a solution. The two mixtures were added together into a volumetric flask and refluxed for 3 hours. Then, it was cooled at room temperature and immersed in ice bath. A mixture was filtered and washed using cold ethanol. The preparation of N-((4-chlorophenyl) carbamothioyl) benzamide [T2] was synthesized with a similar procedure.

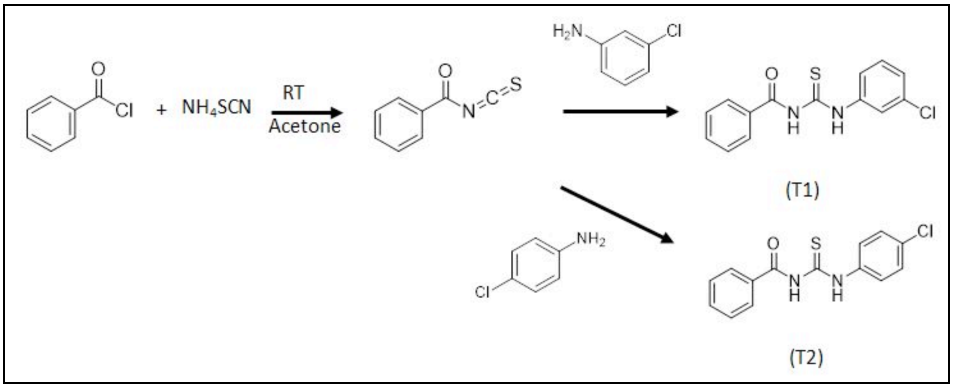


Figure 2. The preparation of (T1) and (T2)

Electrochemical Measurements

A conventional three-electrode system consisting of mild steel as working electrode, platinum as an auxiliary electrode and silver-silver chloride (Ag-AgCl) as reference electrode was used for the measurements. The working electrode of mild steel was allowed to corrode freely in 1M of H_2SO_4 without inhibitor before starting electrochemical measurements and it is open circuit potential (OCP) within 30 minutes (Sundaram & Sundaravadivelu, 2016). The adsorption of inhibitor molecules on the surface of corroding metal using chronoamperometry technique and corrosion study of coated inhibitor on metal using linear polarization resistance technique.

RESULTS AND DISCUSSION

Chemical Analysis

The elemental analysis data of the product shows the relevant frequencies with the expected thiourea as shown in Table 1. The melting point of the ligands was found to be between 138°C – 160°C.

Table 1
Analytical and physical data of the thiourea ligands

Compound	Colour	M.P (°C)	Percentage yield (%)	Elemental analysis data found (calculated) (%)			
				C	H	N	S
T1	White	138-160	83.37	48.65 (57.83)	4.87 (3.81)	12.46 (9.63)	6.34 (11.03)
T2	White	140-155	95.00	55.06 (57.83)	4.42 (3.81)	10.45 (9.63)	7.74 (11.03)

Spectroscopic Studies

Table 2
FTIR spectral data of compounds

Compounds	Major FTIR Absorptions (cm^{-1})			
	C-H	C=O	C=S	C-N
T1	2991.08	1671.00	1256.64	1144.22
T2	3012.79	1533.39	1261.73	1144.81

FTIR Spectroscopy. The T1 and T2 compounds show the important stretching in the FTIR spectra such as *v*(C=S), *v*(C=O), *v*(C-N) and *v*(N-H) which can be observed around 1261 cm^{-1}, 1550 cm^{-1}, 1144 cm^{-1}, 1600 cm^{-1} and 3000 cm^{-1}. Based on the previous studies, it is quite similar among the values reported (Al-Jeilawi, Al-Majidi, & Al-Saadie, 2013). With regards to the carbonyl band, *v*(C=O), T1 were observed at 1671.00 cm^{-1} while for T2 at 1533.39 cm^{-1}. This is due to the presence of aromatic group and the existence of intramolecular hydrogen bonding. For C-N, the absorption band was clearly observed lower than 1200 cm^{-1} whereas in the range 1144 cm^{-1}. While, the C=S absorption band was observed at a range between 1261 cm^{-1} to 1256 cm^{-1}. This band agreed with the results of an earlier study where the type of band was observed at 1271 cm^{-1} (Al-Jeilawi, Al-Majidi, & Al-Saadie, 2013). Furthermore, the reading of the C=S band spectra is a slightly high due to the presence of aromatic group acts as large double bond and lower nucleophilic character of the sulphur atom compared to alkylthioureas.

^{1}H NMR spectroscopy. As shown in Table 3, for both compounds, the resonance for the aromatic group can be observed at 7.0-8.0 ppm. It was found to be a distinctive multiplet resonance because of the unresolved aromatic protons. Meanwhile, the chemical shifts of the amide and thiomide protons for both isomers (T1 and T2) are quite similar. They appeared as a singlet at 9.20 ppm for amide protons and 12.6-12.8 ppm for thiomide respectively. Theoretically, the resonance for this type of group is in the range 12.0 ppm. The downfield of amide protons is mainly due to the formation of the intramolecular hydrogen bonding between the amino proton N−H and the oxygen atom of the carbonyl group which is C=O. Furthermore, all the tested hybrid functional showed relatively good correlation coefficients between the experimental and predicted ^{1}H chemical shifts.

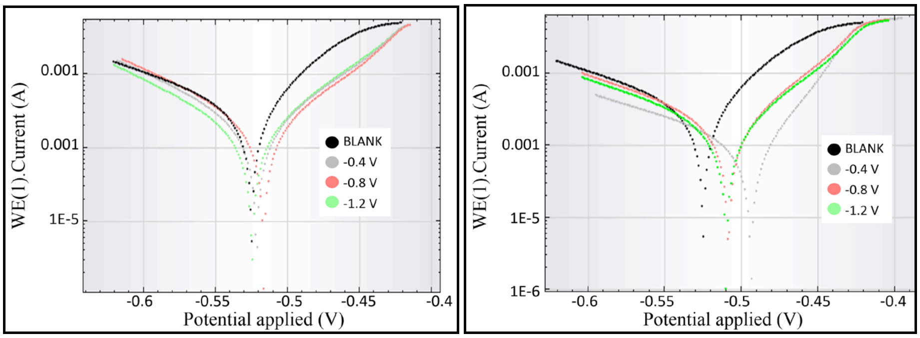
^{13}C NMR spectroscopy. The resonance of aromatic rings, the carbon resonance appeared in the range of 125-132 ppm for both compounds T1 and T2. Meanwhile, for C-Cl carbon resonance was observed in the range of 133-135 ppm. Similarly, the carbon chemical shifts of C=O and C=S are found at 178 ppm and 167 ppm respectively for the both isomers. There is slightly difference in the carbon resonance because they are slightly deshielded due to the formation of intramolecular hydrogen bonding, which increases the electronegativity of oxygen and sulphur atoms. Likewise, to ^{1}H NMR spectra, the isomerization has a slight influence on the position of chemical shift, with chemical shift variations less than 5 ppm.

Corrosion Studies

Linear polarization resistance. In the linear polarization resistance (LPR) technique, the values of change in potential applied as a result of applied potential obtained from electrochemical measurements are used. The data was obtained from the slopes from the initial linear region of the polarization curves of the potential versus current plots. After measuring the currents and potentials, a plot of the parameters measured for mild steel as the working electrode immersed in 1M H_2SO_4 containing same concentrations of thiourea (0.01M) as inhibitor is presented in Figure 3. The percentage of inhibition efficiency (%) was calculated following the formula;

$$\%\ \text{IE} = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}}$$

where i^0_{corr} and i_{corr} are the corrosion current densities of presence and absence of inhibitor in solution respectively.



(a) (b)

Figure 3. The variation of different potential applied and current change for mild steel corrosion in 1M H_2SO_4 in the presence and absence of inhibitor: (a) *N*-((3-chlorophenyl) carbamothioyl) benzamide (T1); and (b) *N*-((4-chlorophenyl) carbamothioyl) benzamide (T2)

Table 3
Electrochemical parameters for mild steel obtained from polarisation curves in 1M H_2SO_4 in the presence of (a) N-((3-chlorophenyl) carbamothioyl) benzamide (T1)

Potential applied (V)	E_{corr} (MV)	β_a (mV/dec)	β_c (mV/dec)	*i*corr µA/cm^2	% IE
0	-525.040	185.570	69.154	408.340	0
-0.4	-521.520	117.950	96.691	241.600	41
-0.8	-516.770	116.690	94.016	243.960	40
-1.2	-524.790	111.640	80.764	183.620	55

Table 4
Electrochemical parameters for mild steel obtained from polarisation curves in 1M H_2SO_4 in the presence of N-((4-chlorophenyl) carbamothioyl) benzamide (T2

Potential applied (V)	E_{corr} (MV)	β_a (mV/dec)	β_c (mV/dec)	*i*corr µA/cm^2	% IE
0	-525.040	185.570	69.154	408.340	0
-0.4	-493.840	140.750	53.532	110.200	73
-0.8	-508.560	145.050	77.717	235.250	42
-1.2	-509.990	156.810	84.548	226.930	44

Based on Tables 3 and 4, throughout the linear polarization technique with differences of potential applied, the highest percentage of inhibition efficiency of T2 is 73% and T1 is 55%. Throughout the data, the icorr which is the current density of mild steel with the presence of difference inhibitors are lower than without it. This indicates that there is an adsorption of inhibitor on mild steel (Fouda & Hussein, 2012) and the presence of aromatic group that have electron density which suppressed the reaction (Wang et al., 1995). It can be observed from the Figure 3 and Table 3, the presence of T1 and T2 drastically reduces the corrosion currents and the corrosion potential shifts to the positive direction. The changes in corrosion potential (E_{corr}) to the positive path direction assumes the presence of inhibitors mostly acting as an anodic inhibitor for mild steel. It is indicated that the inhibition efficiency of both compounds has a positive correlation with same concentration 0.01M of T1 accepted at -1.2 V and 0.01M of T2 accepted at -0.4 V.

Thiourea molecules having a sulphur and two nitrogen atoms which act as donor atoms towards mild steel. The lone pair from these donor atoms are able to transfer electron from the inhibitor onto the metal ((Loto, Loto, & Popoola, 2012). When it forms a covalent bond, the corrosion inhibitor acts as a protective film on the metal. According to this result, the adsorption of inhibitor molecules of T2 is higher than T1 due to differences position of chloride group at *para* and *meta*. The relative yield of T2 is higher than T1, so the chloride group in benzene at monosubstituted benzene is called *ortho, para* directing group. Thus *ortho, para* directing group is electron-donating group, the process of reduction occurred and electron was released for the adsorption metal. The best potential applied for T2 is -0.4 V because it had the highest inhibition efficiency (73%) while for T1, the best potential applied is-1.2 V because of its highest inhibition efficiency (55%).

CONCLUSION

In conclusion, N-((3-chlorophenyl) carbamothioyl) benzamide (T1) and N-((4-chlorophenyl) carbamothioyl) benzamide (T2) was successfully synthesized and fully characterized by spectroscopic methods. The inhibition efficiency of T2 is greater than T1. The greater the inhibition efficiency, the higher the adsorption of inhibitor molecules on mild steel and corrosion process reduces. All the obtained compounds are anodic type of inhibitors.

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