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Synthesis and Preliminary Inhibition Study of Carbonyl Thiourea Derivatives on Corrosion of Mild Steel in Acidic Media

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ABSTRACT

Three new thiourea derivatives compounds namely *N*-benzoyl-*N'*-propylthiourea (TU1), *N*-butanoyl-*N'*-(4-flurophenyl)thiourea (TU2) and *N*-4-chlorobenzoyl-*N'*-(4-flurophenyl)thiourea (TU3), were successfully synthesized and characterized. The micro elemental analysis data, Fourier Transform Infra Red (FTIR), ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra agreed with the predicted structures. The compounds were examined as highly potential corrosion inhibitors for mild steel in acidic media. Their corrosion inhibition property in 1 M hydrochloric acid solution was investigated by using weight loss method with different inhibitor concentrations ranging from 0.0004 M to 0.0001 M for a 7 days exposure. It was found that all compounds were able to retard corrosion of mild steel with the best inhibition to be above 90 % efficiency. The inhibition efficiencies were observed to have increased with increasing concentration of the inhibitors. It is suggested that the compounds adsorb on the surface of the steel forming a protective film which protects the steel from being attacked by the corrosive environment of the acidic media. TU3 with the highest corrosion inhibition property of 96.08 % behaves as highly efficient inhibitor. The difference in corrosion inhibition property of the compounds is due to the different in the structure of the compounds itself.

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INTRODUCTION

Several mineral acid solutions are widely used for various treatments of materials in industry such as pickling, descaling and acid cleaning (Loto *et al*., 2012). They are also used in oil and gas production to stimulate and increase the oil and gas flow, besides to disqualify encrustation in production wells. Among the various acids, hydrochloric acid is accustomed used for this purpose (Gadow and Fouda, 2014). Due to the extremely aggressive nature of the acidic medium, the presence of anticorrosion is essential to keep the surface of substrate metal intact and reduce their corrosion rate.

Corrosion is an electrochemical process that involves deterioration or degradation of metal (Roberge, 2000). This phenomenon results in huge economic losses and possesses many potential safety problems (Yadav *et al*., 2014). The study of corrosion and their inhibition properties is a very active field of research. This corrosion inhibitor is customary used among all other numerous anticorrosion measures, which acts as one of the most economical and effective ways to militate against corrosion.

Most of the efficient inhibitors used are organic compounds having multiple bonds in their molecules, which mainly contain nitrogen and sulphur atoms. Thiourea and its derivatives have been extensively used as corrosion inhibitors for various steels in acidic media by several researchers, such as Torres's *et al* (2014), Uday *et al* (2013) and Abd El-Aziz and Ahmad Hussein (2012). These compounds have shown great effectiveness for inhibiting aqueous corrosion due to film formation on the metal surface. The inhibiting action of these organic compounds is attributed to interactions with metallic surfaces by adsorption. Thiourea and its derivatives are potential corrosion inhibitor because it contains one S and two N atoms. The presence of lone pair of electrons in these atoms, make it easily adsorbed on the metal surface by forming a protective layer and hence reduces the corrosion attack. Moreover, the polar group of the molecule is directly attached to metal and the nonpolar end is oriented in a vertical direction to the metal surface, which repels corrosive species, thus establishing a barrier against chemical

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and electrochemical attack by fluids on the metallic surface (Shetty *et al*., 2006). Other study also states that heterocyclic ring structure which contains nitrogen and oxygen atoms can enhance greater adsorption on metal surface (Chauhan and Gupta, 2009). Hence, cyclic structure of thiourea is the best organic compound that can be used as corrosion inhibitor. The aim of this study is to synthesize and characterize carbonyl thiourea derivatives as shown in Figure 1 and to investigate their inhibition efficiency on corrosion of mild steel in acidic media by using weight loss method.

MATERIALS AND METHOD

Synthesis of N-benzoyl-N'-propylthiourea, (TU1):

An equimolar amount of benzoylchloride in acetone was mixed with ammonium thiocyanate and stirred for 10 minutes. Then, 0.01 mol n-propyl amine in acetone was added to the mixture. The solution was refluxed for 1 hour and then poured into a beaker containing ice cubes. The solid product formed was filtered off and finally recrystallized by using cold ethanol. Yield 72.97%; Brown solid, mp: 131 °C. IR (cm^{-1}): ν(N-H) 3225.5, ν(C=O) 1670.1, ν(C-N) 1257.8, ν(C=S) 871.8. ^{1}H NMR δ 1.0 (s, 3H, CH3); 1.7-1.8 (m, 2H, CH2); 7.28-7.70 (m, Ar-H); 1.277 (s, NH). ^{13}C NMR δ 13.26 (CH3); 22-31 (CH2); 129-138 (aromatic ring); 163 (C=O); 178 (C=S). *Anal*. Calc. (%) For C11H14N2OS: C, 59.46; H, 6.31; N, 12.61; S, 14.41. Found (%): C, 58.92; H, 5.98; N, 12.16.

Synthesis of N-butanoyl-N'-(4-flurophenyl)thiourea, (TU2):

This compound was prepared as mentioned above from equimolar of butyryl chloride and ammonium thiocyanate with 3-fluoroaniline. Yield 80.78%; White solid, mp: 86.5 °C. IR (cm^{-1}): ν(N-H) 3196.1, ν(C=O) 1689.9, ν(C-N) 1264.7, ν(C=S) 950.6. ^{1}H NMR δ 1.03 (s, 3H, CH3); 1.72-1.81 (m, 2H, CH2); 7.50-7.86 (m, Ar-H); 1.26 (s, 2H, NH). ^{13}C NMR δ 11.81 (CH3); 47.55 (CH2); 127-133 (aromatic ring); 166 (C=O); 178 (C=S). *Anal*. Calc. (%) For C13H (a) , 55.0; H, 5.42; N, 11.67; S, 13.33. Foun 24; H, 4.75; N, 11.04.

Synthesis of N-4-chlorobenzoyl-N'-(4-flurophenyl)thiourea, (TU3):

Using the same method as above, this compound was prepared from equimolar amount of 4-chlorobenzoylchloride and ammonium thiocyanate with 3-fluoroaniline. Yield 84.9%; Yellowish-white solid, mp: 123 °C. IR (cm^{-1}): ν(N-H) 3207.4, ν(C=O) 1600.0, ν(C-N) 1350.4, ν(C=S) 846.5. ^{1}H NMR δ 7.28-7.88 (m, Ar-H); 1.87 (s, NH). ^{13}C NMR δ 128-129 (aromatic ring); 166 (C=O); 178 (C=S). *Anal*. Calc. (%) For C14H10N2OFSCl: C, 54.55; H, 3.25; N, 9.09; S, 10.30. Found (%): C, 54.08; H, 2.81; N, 8.94.

Weight loss method:

The mild steel strips were used as the specimens with size of 1 cm x 1 cm. The strips were polished using sandpaper followed by washing in acetone, triple distilled water and dried in air before the initial weight was recorded. The dried strips were tested by immersing them into a corrosion medium of 1 M HCl for a 7 days exposure with and without inhibitors. The inhibitor concentration was varied from 0.0004 M and 0.0001 M. The tested strips were then washed with distilled water and acetone before continued to dry and reweight. The difference in the weight was recorded as the weight loss in milligram, mg.

RESULTS AND DISCUSSION

Synthesis and characterization of carbonyl thiourea derivatives:

The structures of the compounds were established through spectroscopic techniques which are Fourier Transform Infra Red (FTIR), ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR), and CHNS microelemental analysis.

FTIR spectroscopy:

FTIR spectroscopy analysis is one of the most widely used technique to prove the synthesis and possible interactions in organic compounds. FTIR investigation is applied to thiourea derivatives for the determination of molecular structure. TU1, TU2 and TU3 compounds show important stretching in the FTIR spectra such as ν(C=S), ν($C=O_{amide}$), ν(C-N) and ν(N-H) which can be observed around 700 cm^{-1}, 1600 cm^{-1}, 1200 cm^{-1}, and 3000 cm^{-1}, respectively (Roslan *et al*., 2009).

TU1 and TU3 show sharp and strong absorption bands at 3225.5 and 3207.4 cm^{-1} respectively, which attributed to the stretching vibration of N–H group. However, TU2 show a weak and slightly less broad of N-H stretching near 3196.1 cm^{-1}. Basically, there are three major criterias of N-H stretching frequencies (Yusof *et al*., 2010)

Firstly, the force constant for N-H stretching is stronger, secondly, there is a larger dipole moment associated with the N-H bond, and finally, the N-H bond is usually involved in hydrogen bonding. The stronger force constant leads to a higher frequency for absorption. Since the N-H stretching frequency is usually observed around 3500-3100 cm^{-1}, thus, all the three synthesized thiourea derivatives possessed the stretching of N-H peaks.

The larger dipole moment leads to a stronger absorption and the presence of hydrogen bonding has a definite influence on the band shape and frequency position. The presence of hydrogen bonding has two major influences on spectra. First, its presence causes a shift towards lower frequency of all functional groups that are involved in hydrogen bonding and second, the peaks are generally broadened (Yang *et al*., 2007).

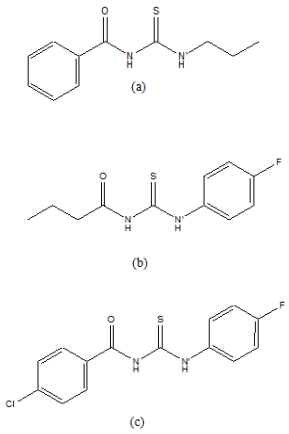

Fig. 1: The chemical structure of the newly synthesized compounds: (a) *N*-benzoyl-*N'*-propylthiourea (TU1), (b) *N*-butanoyl-*N'*-(4-flurophenyl)thiourea (TU2), and (c) *N*-4-chlorobenzoyl-*N'*-(4-flurophenyl)thiourea (TU3).

The peaks appeared in the range of 1680–1630 cm^{-1} were attributed to the absorption of C=O stretching vibration band. Moreover, C=S peaks were observed in the range of 1210–1226 cm^{-1}. In the spectra, there is another intense absorption band at 1050–1250 cm^{-1} corresponding to the C–N fragment. These vibration frequencies occur at variation intensities in IR spectra because of the polarity of the double bond and electron donating groups at ortho, meta or para position of the substituent in the aromatic ring. The characteristic region of the high frequency (C=S) in the aromatic thioureas are described as large double bond character and lower nucleophilic character of the sulphur atom in comparison with alkylthioureas. After all, it can be concluded that the results obtained are in agreement with the literature reported by Alkan *et al*., (2011).

^{1}H and ^{13}C NMR spectroscopy:

The peaks are all corresponded to chemical groups showing the high purity of the compounds. Approximate chemical shift ranges (ppm) for proton spectrum ^{1}H NMR of TU3 showed that proton of amine δH(N) and δH(N') were around 7.28-7.88 ppm. ^{1}H NMR studies in $CDCl_3$ show that δH(N') proton resonance considerably downfield from δH(N) resonance in the spectrum, which may be due to the presence of aromatic group as the substituent in the thiourea compounds.

Meanwhile, chemical shifts for proton δH(phenyl) in all compounds (TU1, TU2 and TU3) were around 7-8 ppm. The chemical shift of this group is variable. It is depends not only on the chemical environment in the molecule, but also on the concentration, temperature and solvent. Generally, the chemical shift of phenyl itself is affected by the type of substituent and its position relative to the considered carbon atom (Breimanaier and Voelter, 1978).

The chemical shift of C=O and C=S carbon resonance for TU3 were clearly observed at 161 ppm and 178 ppm, respectively. There is slightly difference in the carbon resonance because they are slightly deshielded due to the formation of intra molecular hydrogen bonding, increasing electronegativity of oxygen and sulphur atoms and different environment and conformations.

Weight loss method:

In the anticorrosion study by using weight loss method, the inhibition efficiency (IE%) of the synthesized compounds was calculated. The IE of the three synthesized compounds and their respective corrosion rate has been calculated by using equation (1) and (2) as shown below:

$$IE\ \% = \frac{(W_{blank} - W_{inhibitor})}{W_{blank}} \times 100\% \quad (1)$$

where, W_{blank} is the weight loss of mild steel without inhibitor and $W_{inhibitor}$ is the weight loss of mild steel with inhibitor.

$$\text{Corrosion rate} = \frac{\text{Weight loss of mild steel (mg)}}{\text{Surface area of mild steel (dm}^2\text{)} \times \text{Time (days)}} \quad (2)$$

The results obtained are tabulated in Table 1. Figure 2 displays the inhibition efficiency (IE %) versus various inhibitor concentrations (M) of the studied compounds. The corrosion rate for mild steel with the absence and presence of inhibitors is calculated in terms of mg dm^{-2} $days^{-1}$.

Generally, the inhibited mild steel with highest concentration of inhibitor has the lowest corrosion rate (Negm and Zaki, 2008). The statement proves that in this study, the corrosion of the inhibited mild steel occurs much slower in the higher concentration rather than lower concentration. The inhibitor is believed to form a protective layer on the metal surface, hence reduced the corrosion rate. By increasing the inhibitor concentration, the part of metal surface which covered by inhibitor molecules

increases and this leads to an increase in the inhibition efficiencies. From Figure 2, it was observed that the inhibition efficiency increased with increasing concentration of inhibitors. Thus, it can be concluded that, the higher the concentration, the more efficient the thiourea derivatives can protect the mild steel.

In spite of that, by comparing the percentage of inhibition efficiency between the three thiourea derivatives, TU3 has the highest inhibition efficiency of 96.08 % at the concentration of 0.0004 M. On the other hand, the highest inhibition efficiency for TU2 was 93.45 % at concentration of 0.0004 M. Meanwhile, TU1 shows the highest inhibition efficiency at 88.71 % in 0.0004 M. The decrease in concentrations will cause the decrease in the performance of the inhibitors due to the decreasing of inhibition efficiency at low concentration.

From the literature studies, the inhibition efficiency depends on many factors, including adsorption centers, mode of interaction, substituent effect, molecular size and structure of the compounds (El-Egamy, 2008). Thiourea compound is very effective inhibitor for steel in acidic condition due to the presence of sulfur atom which is easily protonated in acidic solution and a stronger electron donor than nitrogen. Therefore, sulfur atom is more strongly adsorbed to the metal surface. It has also been observed that adsorption mainly depends on the presence of π-electrons and hateroatoms, which induced greater adsorption of the inhibitor molecules onto the surface metal. It is believed that the difference in the inhibition efficiency of the ligand in this study is due to the structure of the compounds. It is also suggested that the ligands are attached to the surface of the mild steel at all concentration and decrease the corrosion rate. The effect of highest inhibition efficiency on mild steel for TU3 is due to the presence of two benzene rings with halogen atom attached to each of the ring, thus leads to a greater adsorption on the metal surface as compared to TU2 and TU1.

Conclusion:

Three new thiourea derivatives namely *N*-benzoyl-*N'*-propylthiourea (TU1), *N*-butanoyl-*N'*-(4-flurophenyl)thiourea (TU2) and *N*-4-chlorobenzoyl-*N'*-(4-flurophenyl)thiourea (TU3), were successfully synthesized and characterized using spectroscopic methods. From the anticorrosion study, the synthesized thiourea derivatives (TU1, TU2 and TU3) have been found to display corrosion inhibition properties on mild steel in 1 M HCl. It is believed that these inhibitors form a protective layer on the metal surface and reduce further corrosion attack. The highest inhibition efficiency achieved was 96.08 % found at concentration of 0.0004 M in TU3. Meanwhile, the highest inhibition efficiency of 93.45 % and 88.71 % at the concentration of 0.0004 M were found in TU2 and TU1, respectively. As the concentration of the inhibitors increase, the corrosion inhibition efficiency also increased. TU3 is suggested to be the most efficient inhibitor compared to TU2 and TU1, due to the presence of two benzene rings in the molecule structure. As a conclusion, the corrosion inhibition efficiency of the compound depends on the several factors, such as the presence of electron donating group and pi-electron rich benzene ring in the molecular structure.

Table 1: Parameters of mild steel corrosion activities in 1 M HCl solution with and without inhibitors.

Compound	Concentration (M)	Average weight loss (mg)	Corrosion rate (mg/dm^{-2} $days^{-1}$)	Inhibition efficiency (IE %)
Blank	-	6.790	19.4×10^{-6}	-
TU1	1×10^{-4}	2.694	7.70×10^{-6}	60.31
	2×10^{-4}	1.563	4.47×10^{-6}	76.96
	3×10^{-4}	1.000	286×10^{-6}	85.26
	4×10^{-4}	0.765	2.19×10^{-6}	88.71
TU2	1×10^{-4}	0.562	1.61×10^{-6}	91.70
	2×10^{-4}	0.471	1.35×10^{-6}	93.04
	3×10^{-4}	0.461	1.32×10^{-6}	93.20
	4×10^{-4}	0.443	1.27×10^{-6}	93.45
TU3	1×10^{-4}	0.377	7.71×10^{-5}	94.43
	2×10^{-4}	0.367	7.71×10^{-5}	94.59
	3×10^{-4}	0.342	7.71×10^{-5}	94.95
	4×10^{-4}	0.267	7.71×10^{-5}	96.08

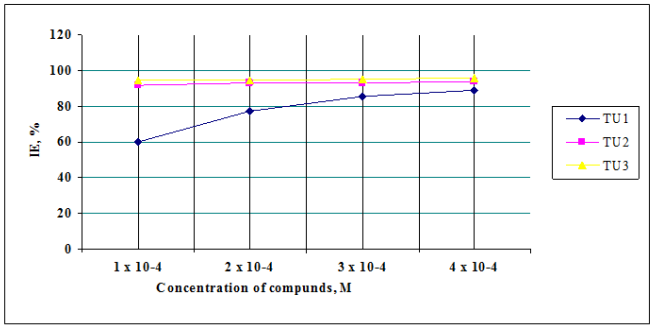

Fig. 2: Graph of concentration of inhibitors versus inhibitory efficiency (IE%).

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