



## SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL STUDIES OF 4-METHOXYBENZOYLTHIOUREA DERIVATIVES

(Sintesis, Pencirian dan Kajian Elektrokimia Terhadap Terbitan 4-Metoksibenzoiltiurea)

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### Abstract

Three new 4-methoxybenzoylthiourea derivatives namely *N*-phenyl-*N'*-4-methoxybenzoylthiourea (A), *N*-(2-methoxy-phenyl)-*N'*-4-methoxybenzoylthiourea (B) and *N*-(2-nitrophenyl)-*N'*-4-methoxybenzoylthiourea (C) has successfully synthesized and characterized by elemental analysis, Fourier Transform Infrared (FTIR), proton (<sup>1</sup>H) and carbon (<sup>13</sup>C) Nuclear Magnetic Resonance (NMR) spectroscopy. Result obtained for IR showed the presence of important bands of the compounds such as  $\nu(\text{N-H})$ ,  $\nu(\text{C=O})$ ,  $\nu(\text{C-N})$  and  $\nu(\text{C=S})$  which were observed at 3200 cm<sup>-1</sup>, 1670 cm<sup>-1</sup>, 1200 cm<sup>-1</sup> and 700 cm<sup>-1</sup>, respectively. The <sup>1</sup>H chemical shifts for CONH and CSNH had been observed around 9 ppm and 12 ppm, respectively. For the <sup>13</sup>C resonance, the signal of C=O and C=S had been observed at 180 ppm and 200 ppm, respectively. The efficiency of the synthesized compounds was investigated as corrosion inhibitor of mild steel in 1.0 M H<sub>2</sub>SO<sub>4</sub> by using linear polarization resistance (LPR) technique.

**Keywords:** 4-methoxybenzoylthiourea, spectroscopy, corrosion inhibitor

### Abstrak

Tiga terbitan 4-metoksibenzoiltiurea iaitu *N*-fenil-*N'*-4-metoksibenzoiltiurea (A), *N*-(2-metoksifenil)-*N'*-4-metoksibenzoiltiurea (B) and *N*-(2-nitrofenil)-*N'*-4-metoksibenzoiltiurea (C) telah berjaya disintesis dan dicirikan dengan penganalisis unsur, spektroskopi infra merah (IR), proton (<sup>1</sup>H) dan karbon (<sup>13</sup>C) resonans magnet nuklear (RMN). Hasil daripada IR menunjukkan kumpulan penting dalam sebatian seperti  $\nu(\text{N-H})$ ,  $\nu(\text{C=O})$ ,  $\nu(\text{C-N})$  and  $\nu(\text{C=S})$  yang terdapat pada 3200 cm<sup>-1</sup>, 1670 cm<sup>-1</sup>, 1200 cm<sup>-1</sup> and 700 cm<sup>-1</sup>. Anjakan kimia <sup>1</sup>H untuk CONH dan CSNH telah dilihat pada 9 ppm dan 12 ppm. Bagi resonans <sup>13</sup>C, C=O dan C=S dapat dilihat pada 180 ppm dan 200 ppm. Keberkesanan sebatian yang disintesis telah dikaji sebagai perencat kakisan keluli lembut dalam 1.0 M H<sub>2</sub>SO<sub>4</sub> dengan menggunakan teknik rintangan polarisasi linear.

**Kata kunci:** 4-metoksibenzoiltiurea, spektroskopi, perencat kakisan

### Introduction

Corrosion prevention by using organic inhibitors is one the most practical ways to protect metal in acidic medium [1]. The studies on it had attracted many attentions of researchers [2,3]. Corrosion inhibitors are substances that may retard or slow down the corrosion rate when added in small concentration to the system. Organic inhibitors containing nitrogen (N), sulphur (S) and oxygen (O) atoms are considered to be the effective and potential corrosion inhibitors [3-6]. The inhibitors that have these atoms in their structure may induce greater adsorption of the

compounds onto the metal surfaces which leads to the formation of a corrosion protecting film. In addition, the stability of the adsorbed inhibitor film on the metal surface also depends on functional groups [9,11,12].

Thiourea and its derivatives were reported to be the potential corrosion inhibitors as compared with other organic compounds because thiourea molecules contain one S atom and two N atoms [6-8]. These atoms act as centre of adsorption that forms a protective layer on the metal surface from the corrosive attack [9-10]. The corrosion inhibition of thiourea is greater in acidic media because this inhibitor acts simultaneously in both anodic and cathodic areas. Thiourea molecules are very effective inhibitors for steel in acidic conditions because S atom is easily protonated in acidic solution and a stronger electron donor than nitrogen [16].

In this study, a series of 4-methoxybenzoylthiourea derivatives with different substituent groups were synthesized and tested as potential corrosion inhibitor in 1.0 M  $\text{H}_2\text{SO}_4$  to achieve inhibition efficiency more than 90%. The effect of different substituent group on the inhibition efficiency at different inhibitors' concentrations were also has been studied.

### Materials and Methods

#### Physical measurement

All reactions were performed under an ambient atmosphere and no special precautions were taken to exclude air or moisture. The chemicals (4-methoxybenzoyl chloride, ammonium thiocyanate, aniline, *o*-Anisidine, 2-nitroaniline) and solvents (acetone and acetonitrile) were purchased from Sigma Aldrich and were used without further purification. Melting points were measured using BÜCHI Melting Point B-545. Infrared spectra were recorded using FTIR Perkin Elmer 100 Spectrophotometer in the spectral range of 4000 to 400  $\text{cm}^{-1}$  by using KBr pellet.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained from Bruker Advance III 300 Spectrometer at room temperature. The elemental analyses of compound were performed by CHNS Analyzer FLASH 2000 series.

#### Synthesis of *N*-phenyl-*N'*-4-methoxybenzoylthiourea (A)

Freshly prepared 5mmol (0.85 g) of 4-methoxybenzoyl chloride in 15 ml acetone was added to equal molar of ammonium thiocyanate (0.38 g). The solution was stirred about 20 min. The precipitate formed was discarded and the solution was kept. An amount of 5 mmol (0.46 ml) of aniline was mixed with the previous solution and undergo refluxed for 3 hours. The solution was poured into a beaker containing ice cubes. The resulting precipitate was collected by filtration, washed ethanol and purified by recrystallization with acetonitrile. Figure 1 show the chemical structure of *N*-phenyl-*N'*-4-methoxybenzoyl thiourea (A).

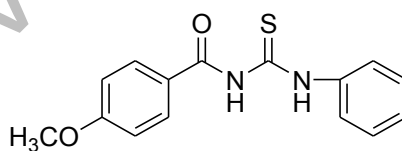


Figure 1. Chemical structure of *N*-phenyl-*N'*-4-methoxybenzoyl thiourea (A)

#### Synthesis of *N*-(2-methoxyphenyl)-*N'*-4-methoxybenzoylthiourea (B)

Similar procedure as the above, this compound was synthesized by reacting 4-methoxybenzoyl chloride (5 mmol, 0.85 g), ammonium thiocyanate (5 mmol, 0.38 g) and *o*-Anisidine (5 mmol, 0.62 g). Figure 2 show the chemical structure of *N*-(2-methoxyphenyl)-*N'*-4-methoxybenzoyl thiourea (B).

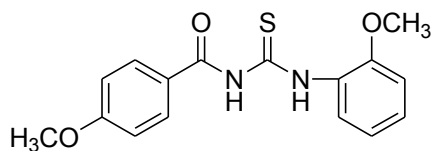


Figure 2. Chemical structure of *N*-(2-methoxyphenyl)-*N'*-4-methoxybenzoyl thiourea (B)

#### Synthesis of *N*-(2-nitrophenyl)-*N'*-4-methoxybenzoylthiourea (C)

This compound was prepared by similar procedure as above with 4-methoxybenzoyl chloride (5 mmol, 0.85 g), ammonium thiocyanate (5 mmol, 0.38 g) and 2-nitroaniline (5 mmol, 0.69 g). Figure 3 show the chemical structure of *N*-(2-nitrophenyl)-*N'*-4-methoxybenzoyl thiourea (C)

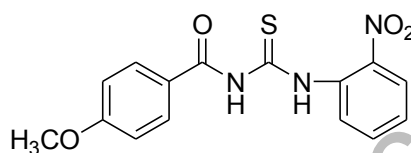


Figure 3. Chemical structure of *N*-(2-nitrophenyl)-*N'*-4-methoxybenzoyl thiourea (C)

#### Linear polarization resistance (LPR) technique

This method was carried out in a three-electrode cells consist of Silver-silver chloride (Ag/AgCl) as a reference electrode, platinum as a counter electrode and the mild steel sample as working electrode. The working electrode was prepared by embedding a rod with a mild steel sample in epoxy resin. The exposed surface area of the sample was 0.065 cm<sup>2</sup>. The measurements by AUTOLAB potentiostat/galvanostat instrument equipped with NOVA software. The polarization curves were recorded at a rate of 0.5 mV s<sup>-1</sup>. Prior to analysis, the working electrode was polished with emery paper, washed with distilled water, dried and finally immersed in the tested solution for an hour to achieve steady state. The tested solution used was sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) with or without compound A, B and C.

#### Results and Discussion

##### Physical measurement

Table 1 shows the percentage yield, colour, melting point and elemental percentage of compound A, B and C. The composition values of the calculated and experimental for elemental analysis are in good agreement. Meanwhile, Table 2 shows the important FTIR adsorption bands, <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts for the three compounds.

Table 1. Percentage yield, colour, melting point and elemental analysis for compound A, B and C

| Compound | Percentage yield (%) | Colour | Melting point (°C) | Elemental analysis (Experimental) (%) |                |                  |                  |
|----------|----------------------|--------|--------------------|---------------------------------------|----------------|------------------|------------------|
|          |                      |        |                    | C                                     | H              | N                | S                |
| A        | 52.9                 | White  | 140                | 62.94<br>(61.00)                      | 4.90<br>(4.92) | 9.79<br>(9.06)   | 11.19<br>(10.42) |
| B        | 63.1                 | White  | 138                | 60.76<br>(60.84)                      | 5.06<br>(4.95) | 8.86<br>(8.56)   | 10.12<br>(9.29)  |
| C        | 58.7                 | White  | 142                | 54.38<br>(59.46)                      | 5.06<br>(4.31) | 12.69<br>(10.87) | 9.67<br>(8.50)   |

Table 2. FTIR absorption bands, NMR proton ( $^1\text{H}$ ) and carbon ( $^{13}\text{C}$ ) shifts for compound A, B and C

| Compound | FTIR             |                   |                  |                   | NMR $^1\text{H}$ |       | $^{13}\text{C}$ |        |
|----------|------------------|-------------------|------------------|-------------------|------------------|-------|-----------------|--------|
|          | $\nu(\text{NH})$ | $\nu(\text{C=O})$ | $\nu(\text{CN})$ | $\nu(\text{C=S})$ | CONH             | CSNH  | C=O             | C=S    |
| A        | 3338.89          | 1655.58           | 1179.81          | 690.91            | 9.07             | 12.80 | 179.20          | 206.97 |
| B        | 3222.93          | 1667.92           | 1221.54          | 712.89            | 9.03             | 12.90 | 179.06          | 207.15 |
| C        | 3247.56          | 1670.21           | 1178.62          | 708.25            | 9.10             | 12.85 | 177.06          | 207.17 |

### Linear polarization resistance

The polarization curves of mild steel in 1.0 M  $\text{H}_2\text{SO}_4$  in the absence and presence of 4-methoxybenzoyl thiourea derivatives are shown in Figures 4 – 6. The corrosion parameters such as corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $i_{\text{corr}}$ ), anodic Tafel slope ( $b_a$ ), cathodic Tafel slope ( $b_c$ ) and inhibition efficiency (IE%) are listed in Table 3. As compared with the  $\text{H}_2\text{SO}_4$  without the presence of any inhibitor or also known as blank, it can be observed that  $i_{\text{corr}}$  decrease in the presence of the inhibitors and decrease as the concentration of the inhibitors increases. The decrease of these values with the presence of inhibitor and increasing inhibitors concentration indicates that there are inhibiting natures of the thiourea derivatives [13,14].

Table 3. LPR parameters of mild steel in 1.0 M  $\text{H}_2\text{SO}_4$  containing different concentrations of A, B and C

| Compound | Concentration (M)  | $b_a$ (V/dec) | $b_c$ (V/dec) | $E_{\text{corr}}$ (V) | $i_{\text{corr}}$ ( $\text{A}/\text{cm}^2$ ) | Corrosion rate (mm/year) | IE % |
|----------|--------------------|---------------|---------------|-----------------------|----------------------------------------------|--------------------------|------|
| Blank    | -                  | 0.1339        | 0.0380        | -0.4287               | 2.02E-04                                     | 2.3425                   | -    |
| A        | $1 \times 10^{-5}$ | 0.0308        | 0.0214        | -0.4119               | 5.83E-05                                     | 0.6767                   | 71.1 |
|          | $1 \times 10^{-4}$ | 0.1138        | 0.0256        | -0.3941               | 5.39E-05                                     | 0.6258                   | 73.3 |
|          | $1 \times 10^{-3}$ | 0.0618        | 0.0208        | -0.3693               | 4.13E-05                                     | 0.47919                  | 79.6 |
| B        | $1 \times 10^{-5}$ | 0.1042        | 0.0349        | -0.4045               | 6.53E-05                                     | 0.7581                   | 67.7 |
|          | $1 \times 10^{-4}$ | 0.0697        | 0.0258        | -0.3944               | 3.48E-05                                     | 0.4036                   | 82.8 |
|          | $1 \times 10^{-3}$ | 0.0570        | 0.0199        | -0.3744               | 2.60E-05                                     | 0.3017                   | 87.1 |
| C        | $1 \times 10^{-5}$ | 0.1282        | 0.0406        | -0.4226               | 0.00012                                      | 1.3890                   | 40.6 |
|          | $1 \times 10^{-4}$ | 0.0665        | 0.0340        | -0.4110               | 6.43E-05                                     | 0.7460                   | 68.2 |
|          | $1 \times 10^{-3}$ | 0.1225        | 0.0460        | -0.3900               | 6.36E-05                                     | 0.7386                   | 77.6 |

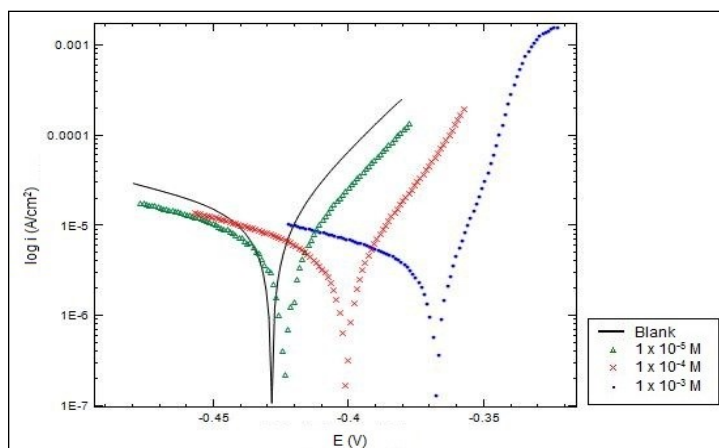


Figure 4. Polarization curves of various concentration of compound A in 1.0 M H<sub>2</sub>SO<sub>4</sub>

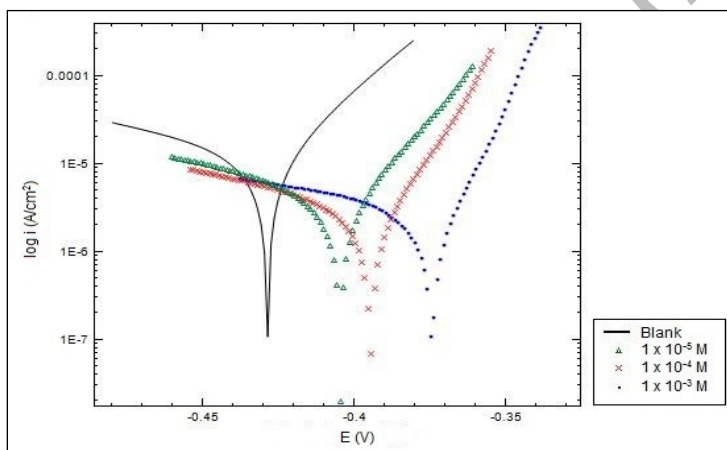


Figure 5. Polarization curves of various concentration of compound B in 1.0 M H<sub>2</sub>SO<sub>4</sub>

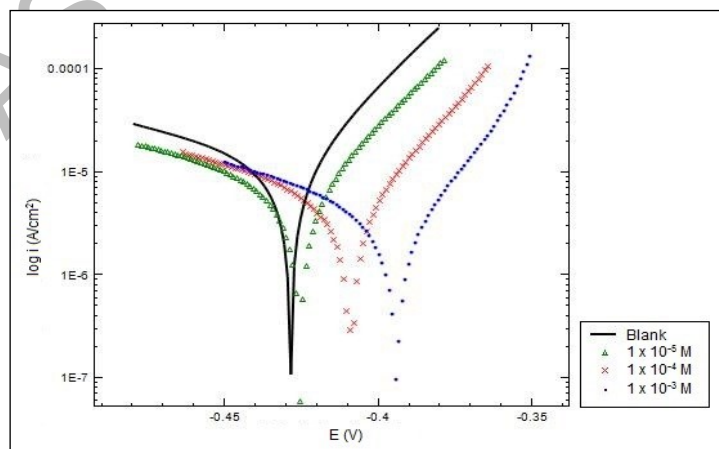


Figure 6. Polarization curves of various concentration of compound C in 1.0 M H<sub>2</sub>SO<sub>4</sub>

From Table 3, the  $E_{\text{corr}}$  values shown slight changes in the presence of the inhibitors. This means that the thiourea derivatives are mixed-type inhibitor in 1.0 M  $\text{H}_2\text{SO}_4$ . In addition, the average displacement of  $E_{\text{corr}}$  is not more than 85 mV, which suggest that these compounds are mixed-type inhibitors [13] even though the polarization curves shift toward the positive side with respect to blank. It also can be observed that the values of  $b_c$  did not change drastically with the addition of the compounds showing that thiourea derivatives did not affect the hydrogen evolution reaction [9]. The changes in  $b_a$  values with the inhibitors concentration shows that may alter the metal dissolution process. Results from this technique shows that the efficiency of these compounds increased as the concentration of corrosion inhibitor increased. The IE% of the inhibitor was calculated based on the  $i_{\text{corr}}$  values obtained from the measurement using the following formula equation 1 [15]:

$$\text{IE \%} = \frac{i'_{\text{corr}} - i_{\text{corr}}}{i'_{\text{corr}}} \quad (1)$$

where  $i'_{\text{corr}}$  and  $i_{\text{corr}}$  are the corrosion current densities in the absence and presence of an inhibitor, respectively.

Among these three compounds, compound B has the highest IE% which is 87.1%. The presence of different substituent in each compounds affect the IE%. Since compound B has methoxy substituent which is classified as electron donating group, it donates electrons to the system and make it electron rich. This enables the compound to form a protective layer on the metal surface. Unlike compound C which posses electron withdrawing group substituent ( $\text{NO}_2$ ), the substituent will withdraw electrons from the system and make it unstable. Thus, forming a less effective layer. The order of the effectiveness of the compounds as corrosion inhibitors are  $\text{B} > \text{A} > \text{C}$ .

### Conclusion

*N*-phenyl-*N*'-4-methoxybenzoylthiourea (A), *N*-(2-methoxyphenyl)-*N*'-4-methoxybenzoylthiourea (B) and *N*-(2-nitrophenyl)-*N*'-4-methoxybenzoylthiourea (C) has been successfully synthesized and characterized. Compound B with methoxy substituent has the highest IE% which is 87.1%. This compound has the potential as an effective corrosion inhibitor that can be used in acid pickling process in chemical or petroleum industries.

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