EFFECT OF SUBSTITUTION OF PHENYL GROUP BY NAPHTYL IN A DIPHENYLTHIOUREA MOLECULE TOWARDS INHIBITION OF CORROSION OF COLD ROLLED STEEL IN 1M HClO$_4$

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Abstract

N, N’-Diphenylthiourea (DPTU) and N-phenyl N’-phenylthiourea (NPTU) synthesized in our laboratory, were tested as inhibitors for the corrosion of cold rolled steel in 1M HClO$_4$ using potentiodynamic polarization and electrochemical impedance measurements. The studies clearly reveal that when we substitutes a phenyl group in N, N’-diphenylthiourea (DPTU) by naphtyl group to obtain N-phenyl N’-phenylthiourea (NPTU), the inhibition efficiency increases from 54 to 93 % at 2 x 10$^{-4}$M of DPTU and 2.5 x 10$^{-4}$ M of NPTU. On the order hand, the results show that DPTU stimulates corrosion at low concentrations. Polarization curves show that NPTU acts as a mixed type inhibitor. Changes in impedance parameters (charge transfer resistance, $R_t$, and double layer capacitance, $C_{dl}$) were indicative of adsorption of NPTU on the metal surface, leading to the formation of a protective film. The degree of the surface coverage of the adsorbed NPTU is determined by ac impedance technique, and it was found that the adsorption of NPTU on the cold rolled steel surface obeys the Langmuir adsorption isotherm. The effect of the temperature on the corrosion behavior with addition of NPTU was studied in the temperature range 25 – 50 °C. Results show that both the rate of corrosion of cold rolled steel and protection efficiency increased with increasing temperature. Activation energies in the presence and absence of NPTU were obtained by measuring the temperature dependence of the corrosion current. Moreover, the free enthalpy of adsorption process was calculated and discussed.

Keywords: N,N’-Diphenylthiourea; N- Naphtyl N’-phenylthiourea; Cold rolled steel; Inhibition corrosion; Perchloric acid.
**Introduction**

Corrosion is a fundamental process playing an important role in economics and safety, particularly for iron and steels. The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media [1-2]. Most well-known acid inhibitors are organic compounds containing nitrogen, sulfur and oxygen atoms. Among them, the thiourea and its derivatives have been studied as interesting organic inhibitors for corrosion for iron and steel [3,4].

The synthesis of new organic molecules offers different molecular structures containing several heteroatoms and substituents. Their adsorption is generally explained by the formation of an adsorptive film of a physical or chemical character on the metal surface. It has been suggested that chemisorbed molecules protect anodic areas and reduce the inherent reactivity of the metal at the sites where they are attached, where as physisorbed molecules are attached to metal at local cathodes and essentially retard metal dissolution by stifling the cathodic reaction [5,6].

In this paper, we have studied the effect of the addition of N,N’-diphenylthiourea (DPTU) and N-naphtyl N’-phenylthiourea (NPTU) on the corrosion inhibition of cold rolled steel in 1M HClO\textsubscript{4} using potentiodynamic polarization and electrochemical impedance spectroscopy. The choice of these compounds is based on molecular structure considerations.

**2. Experimental**

**2.1. Materials**

Cold rolled steel composed of (wt.%): C ≤ 0.15%, Mn ≤ 0.30%, Si ≤ 0.20%, P ≤ 0.03%, S ≤ 0.03% and the remainder iron was used as the working electrode for all studies.

Inhibitors were synthesized in the laboratory by condensation of phenyl isothiocyanate with appropriate amine and were purified and analyzed by IR and NMR spectroscopies before use. Fig.1 shows the molecular structures of the investigated organic compounds which have been labeled DPTU and NPTU. The acid solutions were made from AR grade HClO\textsubscript{4}. Appropriate concentration of acid was prepared by using double-distilled water.
2.2. Electrochemical measurements

Electrochemical experiments were carried out in a glass cell (CEC / TH-Radiometer) with a capacity of 500 ml. A platinum electrode and a saturated calomel electrode (SCE) were used as a counter electrode and a reference electrode. The working electrode (WE) was in the form of a disc cut from mild steel under investigation and was embedded in a Teflon rod with an exposed area of 0.5 cm\(^2\).

Electrochemical impedance spectroscopy (EIS), potentiodynamic and linear polarization were conducted in an electrochemical measurement system (VoltaLab40) which comprises a PGZ301 potentiostat, a personal computer and Volta Master 4 and Zview software.

The a.c. impedance measurements were performed at corrosion potentials (\(E_{\text{corr}}\)) over a frequency range of 10 kHz - 20 mHz, with a signal amplitude perturbation of 10 mV. Nyquist plots were obtained.

The corrosion current densities were determined by Tafel extrapolation of the cathodic curves to the open circuit corrosion potentials.

Inhibition efficiencies \(P\%\) were calculated as follows:

- For potentiodynamic polarization measurements:

\[
P \% = \frac{I_{\text{corr}} - I'_{\text{corr}}}{I_{\text{corr}}} \times 100
\]  

(1)

where \(I_{\text{corr}}\) and \(I'_{\text{corr}}\) are the corrosion current densities in the absence and the presence of the inhibitor.

- For impedance measurements:

\[
P \% = \frac{R'_1 - R_1}{R'_1} \times 100
\]  

(2)
where $R_t$ and $R'_t$ are the charge transfer resistance values without and with inhibitor, respectively.

3- Result and discussion
3.1. Polarization curves

Figs. 2 - 3 depict the anodic and cathodic polarization curves recorded on cold rolled steel in 1 M HClO$_4$ at different concentrations of NPTU and DPTU at 30°C. We remark that DPTU at lower concentrations up to $2 \times 10^{-4}$ M accelerates anodic reactions, and thus stimulate corrosion.

![Polarization curves](image)

**Figure 2.** Potentiodynamic polarisation curves for cold rolled steel in 1 M HClO$_4$ Containing different concentrations of DPTU at 30°C.

The electrochemical parameters derived from these curves are given in Table 1. It can be seen from this table that DPTU act as corrosion stimulator and the acceleration of corrosion of cold rolled steel is greater at lower concentrations that at higher concentrations of this compound. This indicates that the DPTU compound, in 1 M HClO$_4$, has a catalytic effect on the rate of steel dissolution. According to Oldham [7] the catalytic effect of this compound can be due to change in the oxidation state of the sulfur atom, which is easily oxidized in acid and thus the inhibiting effect uncertain.
On the contrary, NPTU hindered the acid attacks on the steel electrode. The polarization curves show that this inhibitor does not affect the cathodic slopes ($b_c$). This indicates that the addition of NPTU does not modify the mechanism of the proton discharge reaction. Fig. 3 shows also that NPTU exhibits both cathodic and anodic inhibition effects but the cathode is more preferentially polarized.

A number of significant kinetic parameters are listed in table 1. The cathodic current densities ($I_{corr}$) are determined by extrapolation of the cathodic Tafel lines to the corrosion potential. The results suggest that the addition on NPTU enhances inhibition at all concentrations. As the concentration increase inhibitor efficiency increases as well. On the other hand, this indicates that NPTU does not decompose in 1M HClO$_4$. Stabilizing effect that comes from the substitution of phenyl group by naphtyl group indicates rearrangement of the charge density inside the molecule, thus shows the corrosion inhibition of NPTU at all concentrations.

**Figure 3.** Potentiodynamic polarisation curves for cold rolled steel in 1 M HClO$_4$ containing different concentrations of NPTU at 30°C.
Table 1  Electrochemical parameters and the corresponding corrosion inhibition efficiencies for the corrosion of cold rolled steel in 1M HClO\textsubscript{4} containing different concentrations of NPTU, and DPTU at 303 K

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>-(E_{\text{corr}}) (mV/SCE)</th>
<th>(I_{\text{corr}}) ((\mu\text{A cm}^{-2}))</th>
<th>(b_c) (mV dec(^{-1}))</th>
<th>(P_I) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>432</td>
<td>489</td>
<td>153</td>
<td>----</td>
</tr>
<tr>
<td>5 \times 10^{-5}</td>
<td>468</td>
<td>112</td>
<td>145</td>
<td>77.1</td>
</tr>
<tr>
<td>7.5 \times 10^{-5}</td>
<td>452</td>
<td>57</td>
<td>159</td>
<td>88.3</td>
</tr>
<tr>
<td>NPTU</td>
<td>1 \times 10^{-4}</td>
<td>460</td>
<td>38</td>
<td>150</td>
</tr>
<tr>
<td>2 \times 10^{-4}</td>
<td>450</td>
<td>36</td>
<td>152</td>
<td>92.6</td>
</tr>
<tr>
<td>5 \times 10^{-5}</td>
<td>584</td>
<td>1585</td>
<td>157</td>
<td>-69.1</td>
</tr>
<tr>
<td>1 \times 10^{-4}</td>
<td>572</td>
<td>830</td>
<td>155</td>
<td>-41.1</td>
</tr>
<tr>
<td>DPTU</td>
<td>2 \times 10^{-4}</td>
<td>588</td>
<td>521</td>
<td>157</td>
</tr>
<tr>
<td>5 \times 10^{-4}</td>
<td>548</td>
<td>251</td>
<td>130</td>
<td>48.7</td>
</tr>
</tbody>
</table>

3.2. Electrochemical impedance spectroscopy

The corrosion behavior of cold rolled steel in 1 M HClO\textsubscript{4} in the absence and the presence of NPTU and DPTU was investigated by EIS at 30°C after immersion of 1 h. Impedance spectra for cold rolled steel in the presence of all concentrations of the compounds are similar in shape. Figs. 4 - 5, depict the Nyquist plots that exhibit one semicircle, which centre lies under the abscissa. To describe the observed depression of the capacitive semicircle it is necessary to replace the capacitor by some element, which has frequency dispersion like the constant phase element (CPE). This element is a generalized tool, which can reflect exponential distribution of the parameters of the electrochemical reaction related to energetic barrier at charge and mass transfer, as well as impedance behavior caused by fractal surface structure.. The impedance of the CPE is [8-10]:

\[ Z_{\text{CPE}} = Q^{-1} (j\omega)^{-n} \]  \hspace{1cm} (3)

where Q is a proportionality coefficient and n an exponent related to the phase shift. For whole numbers of n = 1, 0, -1, CPE is reduced to the classical lumped elements capacitor (C),
resistance (R) and inductance (L), respectively. The value of n = 0.5 corresponds to Warburg impedance (W). Values of n can serve as a measure of the surface heterogeneity [8, 11].

**Figure 4.** Nyquist plots for cold rolled steel in 1 M HClO$_4$ containing different concentrations of DPTU at 30°C.

**Figure 5.** Nyquist plots for cold rolled steel in 1 M HClO$_4$ containing different concentrations of NPTU at 30°C.
Thus the equivalent circuit model employed for these systems is presented in Fig. 6.
The resistance $R_s$ is the resistance of the solution; $R_t$ reflects the charge transfer resistance and CPE has the meaning of a frequency distributed double - layer capacitance.

**Figure 6.** The equivalent circuit of the impedance spectra obtained for NPTU and DPTU.

The impedance parameters for the corrosion of cold rolled in 1 M HClO$_4$ without and with addition of various concentrations of NPTU and DPTU are given in Table 2.

<table>
<thead>
<tr>
<th>Conc. (M)</th>
<th>$R_t$ (Ω cm$^2$)</th>
<th>$Q$ (Ω$^{-1}$ cm$^{-2}$ s$^n$)</th>
<th>$n$</th>
<th>$C_{dl}$ (µF cm$^{-2}$)</th>
<th>$P$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>59</td>
<td>$2.18 \times 10^{-5}$</td>
<td>0.85</td>
<td>103</td>
<td>-----</td>
</tr>
<tr>
<td>5 × 10$^{-5}$</td>
<td>208</td>
<td>$4.84 \times 10^{-5}$</td>
<td>0.87</td>
<td>24.3</td>
<td>71.6</td>
</tr>
<tr>
<td>NPTU</td>
<td>7.5 × 10$^{-5}$</td>
<td>368</td>
<td>$4.66 \times 10^{-5}$</td>
<td>0.86</td>
<td>24.0</td>
</tr>
<tr>
<td>1 × 10$^{-4}$</td>
<td>450</td>
<td>$3.16 \times 10^{-5}$</td>
<td>0.84</td>
<td>14.0</td>
<td>86.9</td>
</tr>
<tr>
<td>2.5 × 10$^{-4}$</td>
<td>881</td>
<td>$2.50 \times 10^{-5}$</td>
<td>0.81</td>
<td>10.2</td>
<td>93.3</td>
</tr>
<tr>
<td>5 × 10$^{-5}$</td>
<td>8</td>
<td>$18.8 \times 10^{-5}$</td>
<td>0.87</td>
<td>71.2</td>
<td>-86.4</td>
</tr>
<tr>
<td>1 × 10$^{-4}$</td>
<td>33</td>
<td>$5.2 \times 10^{-5}$</td>
<td>0.90</td>
<td>25.6</td>
<td>-44.1</td>
</tr>
<tr>
<td>DPTU</td>
<td>2 × 10$^{-4}$</td>
<td>55</td>
<td>$3.6 \times 10^{-5}$</td>
<td>0.87</td>
<td>14.2</td>
</tr>
<tr>
<td>5 × 10$^{-4}$</td>
<td>170</td>
<td>$7.2 \times 10^{-5}$</td>
<td>0.86</td>
<td>35.0</td>
<td>65.3</td>
</tr>
</tbody>
</table>

It is found that DPTU accelerate the corrosion of cold rolled steel at different concentrations up to 2 x 10$^{-4}$. This is clearly evident from impedance experiments. High values of $C_{dl}$ and low values of $R_t$ are obtained for 1 M HClO$_4$ in the presence of this compound due to the corrosion acceleration. On the other hand, the values of $n$ in the presence of this compound are higher than in 1 M HClO$_4$ (0.85). This is an indication that the stimulator can also
contribute to some decrease of the surface heterogeneity, probably because they facilitate the dissolution of the most active surface sites [12]. Concerning NPTU, it is found from Table 2, that as NPTU concentration increased the \( R_t \) values increased as well, but the \( C_{dl} \) values tended to decrease. The greatest effect was observed at a concentration of \( 2.5 \times 10^{-4} \) M, which produces \( R_t \) value of 881 \( \Omega \cdot \text{cm}^2 \). The decrease in \( C_{dl} \) values was due to the adsorption of NPTU on the metal surface. The decrease of the values of \( n \) when compared with 1 M HClO\(_4\) and with concentration can be explained by some increase of surface heterogeneity, due to the adsorption of the inhibitor on the most active desorption sites [11].

The excellent behavior of NPTU previously evidenced in the potentiodynamic polarization measurements was again confirmed.

Note that the capacitances were calculated from \( Q \) and \( R_t \) using the equation [13, 14]:

\[
Q = \left( \frac{C R_t}{R_t} \right)^n
\]

(4)

3.3. Adsorption isotherm

It is known that the adsorption isotherms are very important for the understanding of the mechanism of corrosion inhibition [15]. The most frequently used isotherms are Langmuir, Freundlich, Temkin, Frumkin, etc. Assuming a direct relationship between inhibition efficiency and surface coverage, the degree of surface coverage, \( \theta \), of the metal surface was calculated from potentiodynamic polarization measurements using the following relation [16]:

\[
\theta = \frac{I_{\text{corr}}' - I_{\text{corr}}}{I_{\text{corr}}}
\]

(5)

where \( I_{\text{corr}} \) and \( I_{\text{corr}}' \) are the current densities for the blank and the inhibited solutions, respectively.

The surface coverage values (\( \theta \)) were tested graphically to allow fitting of a suitable adsorption isotherm. The plot of \( C/ \theta \) versus \( C \) (Figure 7) yielded straight lines with slopes equal to 1.03 NPTU at 30 °C, clearly proving that the adsorption of the NPTU from 1 M HClO\(_4\) solution on the cold rolled steel obeys the Langmuir adsorption isotherm where,

\[
\theta = \frac{KC}{KC + 1}
\]

(6)

with
\[ K = \left( \frac{1}{55.5} \right) \exp \left( \frac{-\Delta G_{\text{ads}}}{RT} \right) \]  

(7)

where \( K \) is the equilibrium constant for the adsorption process, \( C \) is the concentration of the inhibitor and \( \theta \) is the surface coverage.

Figure 7. Curves fitting of the corrosion data of cold rolled steel in the presence of NPTU to Langmuir isotherm at 30 °C.

The value of equilibrium adsorption constant obtained from this isotherm is \( 1.06 \times 10^{5} \) M\(^{-1}\) for NPTU at 30°C, suggesting a chemically adsorbed film [17]. This is in good agreement with values of inhibition efficiency obtained from the electrochemical measurements. Therefore, inhibition efficiency increases with increasing equilibrium constant. Moreover, the largest negative values of \( \Delta G_{\text{ads}} \), i.e. -39.25 kJ / mol for NPTU, indicate that this inhibitor is strongly adsorbed onto the cold rolled steel surface.

We can note that a plausible mechanism of corrosion inhibition of cold rolled steel in 1 M HClO\(_4\) for NPTU may be deduced on the basis of adsorption. In acidic solutions, this inhibitor can exist as cationic species which may be adsorbed on the cathodic sites of the cold rolled steel and reduce the evolution of hydrogen. Moreover, the adsorption of these compounds on anodic sites through lone pairs of electrons of nitrogen, and sulfur atoms and through \( \pi \)-electrons of C=S, phenyl and naphtyl groups will then reduce the anodic dissolution of cold rolled steel.
3.4. Effect of temperature

The effect of temperature variation on inhibitor efficiency is important in practical applications. It is essential therefore to study this in order to obtain an indication of the inhibitive efficiency at height temperature as well as at room temperature.

The behavior of cold rolled steel in 1 M HClO₄ aqueous solution in the absence and in the presence of NPTU at $2.5 \times 10^{-4}$ M during polarization was studied in the 298 -323 K temperature ranges. The corresponding data are given in Table 3.

We remark that the rise in temperature leads to an increase in corrosion rate with and without inhibitors. It can be seen from Table 3 that the inhibitor efficiencies increase with temperature.

<table>
<thead>
<tr>
<th>C (M)</th>
<th>T (K)</th>
<th>$-E_{corr}$ (mV / SCE)</th>
<th>$I_{corr}$ (µA cm⁻²)</th>
<th>$b_\alpha$ (mV dec⁻¹)</th>
<th>P(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>298</td>
<td>432</td>
<td>209</td>
<td>173</td>
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</tr>
<tr>
<td></td>
<td>303</td>
<td>435</td>
<td>489</td>
<td>153</td>
<td>----</td>
</tr>
<tr>
<td></td>
<td>313</td>
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<td>1620</td>
<td>168</td>
<td>----</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>463</td>
<td>4256</td>
<td>166</td>
<td>----</td>
</tr>
<tr>
<td>2.5 x 10⁻⁴</td>
<td>298</td>
<td>452</td>
<td>18</td>
<td>150</td>
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<td>56</td>
<td>155</td>
<td>96.5</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>452</td>
<td>80</td>
<td>159</td>
<td>98.2</td>
</tr>
</tbody>
</table>

The activation energy can be determined from Arrhenius plots for cold rolled steel presented in Figure 8 by the following relation:

\[
\ln I_{corr} = \frac{-E_A}{RT} + \ln A \tag{8}
\]

where $E_A$ represent the apparent activation energy, $R$ is the universal gas constant, $T$ is the absolute temperature and $A$ is the pre-exponential factor.

The regression between $\ln I_{corr}$ and $1/T$ was completed by using computer, and it is found that the regression coefficients are very close to 1, which means that the linear relationship between $\ln I_{corr}$ and $1/T$ is good.

The apparent activation energies for the corrosion in the absence and presence of NPTU can be calculated from the slopes of the regression and are respectively:
We remark the decrease in activation energy in the presence of the inhibitor studied. The influence of temperature on corrosion inhibition was studied by several authors [18-20] who reported that the activation energy is lower for the inhibited than for the uninhibited reaction. This was attributed to increased surface coverage of the metal surface with the inhibitor molecule with increasing temperature. On the other hand, the decrease in $E_A$ in inhibited solution supports the assumption for chemisorption of the inhibitor on the metal surface [21]. Moreover, Szauer, Brandt and Foroulis [22,23] declare that the lower activation energy value of the process in the presence of the inhibitor compared to that of in its absence is attributed to its chemisorption, while the opposite is the case with physical adsorption.

Table 3 shows also that the inhibition efficiency ($P\%$) increases with the increase of the temperature of corrosion medium. This result can be explained by the characteristics of the cathodic process of hydrogen evolution in acidic solutions. The hydrogen evolution overvoltage decreases with increasing temperature that leads to increase in the cathodic reaction rate. On the other hand, temperature increase accelerates the chemisorption of the inhibitor of the metal surface. When the latter effect is predominant, the final result is an increase of the inhibiting effect, which is observed in this work.
Conclusions

- DPTU acts as corrosion stimulator and the acceleration of corrosion of cold rolled steel is greater at lower concentrations that at higher concentrations of this compound.
- The addition on NPTU enhances inhibition at all concentrations. As the concentration increases inhibitor efficiency increases as well.
- NPTU exhibits both cathodic and anodic inhibition effects but the cathode is more preferentially polarized.
- Good agreement was obtained between the potentiodynamic polarisation measurements and the electrochemical impedance spectroscopy technique.
- The adsorption of NPTU onto cold rolled steel surface accords with the Langmuir adsorption isotherm.
- Chemisorption of NPTU is evident from, the apparent activation energy of the corrosion that is lower in presence of NPTU than in its absence, the increase in inhibition efficiency with temperature and the large negative values of $\Delta G_{\text{ads}}^\circ$.

References


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concentration and temperature of the corrosion medium on their protective action,


