ELECTROCHEMICAL CORROSION OF LOW CARBON STEEL IN A HYDROCHLORIC ACID MEDIUM

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ABSTRACT

Inhibition is one of the mechanisms used for mitigating the metallic corrosion, particularly in an acid environment. The present work aims to investigate the inhibiting effect of N-benzyl-N’-phenyl thiourea (BPTU) on the corrosion of low carbon steel in a 0.1 M hydrochloric acid (HCl) solution using a Tafel extrapolation and linear polarization techniques. The study reveals that BPTU acts as an excellent anodic inhibitor for low carbon steel in a HCl solution. The protective efficiency of the compound was found to be more than 97% even at higher temperatures. The study demonstrated that BPTU gets adsorbed on the steel surface, following Temkin’s adsorption isotherm and the inhibition is controlled by a chemisorption mechanism. The investigation shows that the results obtained from the Tafel extrapolation and linear polarization techniques for the corrosion of mild steel in HCl medium were in good agreement. The influence of temperatures and concentrations of BPTU on the corrosion of low carbon steel are also examined in the present work.

Keywords: Activation energy; Corrosion; Chemisorption; Hydrochloric acid; Low carbon steel; Polarization

1. INTRODUCTION

Inhibitors are the substances which when added in small quantity to the corrosive medium, decrease the rate of reactions in metal with the medium (Anand & Balasubramanian, 2015). The use of inhibitors in an acidic environment is most economical and a trouble-free surface coating technique for giving protection against corrosion and for improving the corrosion resistance of the metals and alloys (Bentiss et al., 2000; Al-Otaibi et al., 2014; Rizkia et al., 2015). The inhibitors adsorbed on the surface of the metal by forming a thin film and decreases corrosion by decreasing the electrochemical reactions or by increasing the polarization behavior of anode or cathode (Mora-Mendoza et al., 2002; Nik et al., 2010). Low carbon steel is a well known material which is widely used in various industries, such as power plants, transportation, chemical processing, pipe lines, mining, construction etc., and comes in contact on a recurrent basis with aqueous solutions (Nik et al., 2011). Therefore, many researchers have shown keen interest in investigating the corrosive behavior of low carbon steel in an acid environment. Among the mineral acids, hydrochloric acid is generally used in pretreatment of metallic components (Hudson & Warning, 1980; Kaan Emregul & Hayvali, 2006).

Temperature is one of the key parameters which greatly influence the inhibition process of metals and alloys, especially in aqueous environment. Corrosion is more spartan in pickling and
cleaning operations at higher temperatures; hence, special attention must be taken while selecting inhibitors for preventing further dissolution of metals (Al-Mayof et al., 2001). Inhibitors used in the corrosion process are expected to work efficiently at low concentrations and high temperatures and also should be thermally and chemically stable (Schmitt, 1980). The majority of the inhibitors used for mitigating the effects of acid corrosion in the manufacturing sector are organic compounds mainly encompassing N, S and O atoms through which inhibitors get adsorbed on the surface of the metal. Among these, thiourea $\text{CS(NH}_2\text{)}_2$ and its derivatives are widely used as corrosion inhibitors (Frighani et al., 1988; Singh, 1993; Agarwal & Namboodhiri, 1990).

From the literature, it is observed that “substituents to thiourea increase further its electron densities for their adsorption on the metal surface” (Shetty et al., 2006). Hence, in the present work, an attempt has been made to synthesize $\text{N-benzyl-N’-phenyl thiourea}$ to predict the inhibiting action of this compound on the corrosion of low carbon steel in a 0.1N HCl solution at different temperatures and inhibitor concentrations by using a Tafel extrapolation and linear polarization techniques. The selection of this compound was based on the fact that it can be synthesized conveniently from relatively cheap raw materials and the compound seems to be environmentally friendly.

A Tafel extrapolation for a metal specimen can be obtained by polarizing the specimen to about ± 250 mV from the rest potential, as shown in Figure 1.

![Figure 1 Schematic representation of anodic and cathodic polarization curves](image)

Extrapolation of the linear portion of the curve representing the Tafel region in either a cathodic or anodic polarization curve to the corrosion potential will give the corrosion current density ($i_{\text{cor}}$) which can be used to calculate the corrosion rate. The principle of a linear polarization method is that within 20 mV, the metals are either more noble (less active cathodic) or more active (anodic) than the corrosion potential. It is observed that the applied current density is a linear function of the electrode potential. This is illustrated in Figure 2, where the corrosion potential is used as an over voltage reference point and a plot of over voltage versus applied anodic and cathodic current is shown in the linear scale (Fontana, 1987; Rajnarayan, 1993).

Corrosion problems were found in all aspects of technology, resulting in high cost. Therefore, a comprehensive research and development program needs to be carried out to reduce the damage due to corrosion. It is well known that low carbon steel has extensive applications in the different manufacturing sectors and it is more susceptible to corrosion, especially in an acid
environment. In this context, the authors aim to synthesize a novel inhibitor, N-benzyl-N'-phenyl thiourea for investigating the corrosive behavior of low carbon steel in a HCl solution.

Figure 2 Schematic representation linear polarization curve

2. EXPERIMENTAL

2.1. Specimen Preparation
The mild steel specimen of chemical composition (Wt%): C: 0.205; Si: 0.06; Mn: 0.55; S: 0.047; P: 0.039 and balance Fe was used for measuring the rate of corrosion in a HCl medium in the absence and presence of BPTU (green carbons). The bottom surface area (0.786 cm²) of the specimen was polished with emery papers of different grades, thoroughly cleaned with soap and water and then rinsed with distilled water and finally dried in air. Then, the bottom surface of the specimen was exposed to the corroding medium for conducting electrochemical studies. The microstructure of the mild steel specimen used for electrochemical studies is shown in Figure 3.

Figure 3 Microstructure of low carbon steel specimen

2.2. Inhibitor Preparation
The compound N-benzyl-N'-phenyl thiourea was synthesized by referring to the reported procedure of synthesizing the thiourea derivatives (Moore & Crossly, 2003). The compound was purified by ethanol and its purity was tested by elemental analysis, which is shown in Table 1.
Table 1 Elemental analysis of the compounds studied

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Molecular formula</th>
<th>Calculated (Found) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPTU</td>
<td>C₁₄H₁₄N₂S</td>
<td>C: 69.39 (69.26) H: 5.82 (5.79) N: 11.56 (11.60) O: 13.23 (13.19)</td>
</tr>
</tbody>
</table>

The molecular weight and the melting point of the compound investigated were 242.34 grams/mol and 158°C, respectively. The molecular structure of the compound studied is given in Figure 4. AR grade HCl and distilled water were used for preparing 0.1 M HCl solution for experimental work.

2.3. Polarization Studies

Polarization studies were carried out in the presence and absence of BPTU using a Wenking potentiostat (LB95L) and a three electrode cell containing 400 ml of electrolyte. Platinum foil was used as an auxiliary electrode and a saturated calomel electrode (SCE) is used as reference electrode. The steady state open circuit potential (OCP) with respect to the saturated calomel electrode was noted, and it will be presented at the end of 25- to 30-minute session. The corrosion rates were determined by using linear polarization and Tafel extrapolation methods. The experimental setup used for polarization studies is shown in Figure 5.

2.4. Tafel Extrapolation Technique

Tafel extrapolation studies were performed from OCP-250 mV to OCP+250 mV with a scanning rate of 20 mV/min from the cathodic side and the corrosion currents were noted for room temperature (28°C) in the absence and presence of BPTU. The corrosion current density ($i_{corr}$) and corrosion potential ($E_{corr}$) were obtained by extrapolating the Tafel region of the plot of potential verses log I. The experiments were repeated at 40°C and 50°C. The temperatures were accurately maintained within ± 1°C and the results were also cross-checked by using a linear polarization method. The corrosion rate (CR) was estimated with Equation 1.
Corrosion rate (CR), mpy = \frac{(0.129 \times Eq.Wt \times i_{corr})}{D} \tag{1}

where, \(i_{corr}\) is the corrosion current density in \(\mu A/cm^2\), Eq. Wt is the equivalent weight of the specimen (taken as 27.925 grams) and D is the specimen density taken as 7.86 g/cc. The percentage inhibition efficiency (\%IE) or the protective efficiency and the degree of surface coverage (\(\theta\)) will be determined with help from distant relations, as shown in Equation 2.

\[
\%IE = \left[ \frac{(i_{corr} - i_{corr(inh)})}{i_{corr}} \right] \times 100
\]

\(\%IE\) is the current density in the absence of an inhibitor and \(i_{corr(inh)}\) is the current density in the presence of inhibitor as shown in Equation 3.

\[
\theta = \left[ \frac{(i_{corr} - i_{corr(inh)})}{i_{corr}} \right]
\]

\(2.5. \) Linear Polarization Method

Linear polarization studies were conducted in the potential (E) range of -20 mV versus OCP to +20 mV versus OCP with a scanning rate of 5 mV / min from the cathodic side and steady state corrosion currents (I) were noted. The plot of E versus I was drawn and the slope of E versus I curve was used to determine the corrosion current density (\(i_{corr}\)) and the corrosion rate (CR) as follows in Equations 4 and 4.1:

\[
i_{corr} = 0.026 / \text{slope} \tag{4}
\]

\[
Corrosion \ rate (CR), \ mpy = \frac{(0.129 \times Eq.Wt \times i_{corr})}{D} \tag{4.1}
\]

where, \(i_{corr}\) is the corrosion current density in \(\mu A/cm^2\), equivalent, Wt is the specimen equivalent weight (taken as 27.925 grams), D is the specimen density taken as 7.86 g/cc.

\(3. \) RESULTS AND DISCUSSION

Organic inhibitors have wide application in industries, especially in an acidic environment. The inhibition of corrosion is generally described as the interface of a foreign substance to the corrosive medium with corrosion reactions, and it is visualized that such interface takes place through the adsorption of the inhibitor on the metal surface. All corrosion reactions are electrochemical in nature. This implies the existence of simultaneous anodic and cathodic currents of equal magnitude across the interface of the metal. In the present study, a Tafel extrapolation and linear polarization studies were conducted to examine the effect of BPTU on the corrosion behaviour of low carbon steel in a 0.1 M HCl medium with different concentrations of BPTU and at different temperatures. The results of electrochemical studies are given in Tables 2 and 3, and Figure 6 illustrates the Tafel plots for low carbon steel in a HCl medium in the presence and absence of 0.0004 m/L of BPTU at different temperatures.
Table 2 Tafel extrapolation results for low carbon steel in 0.1 M HCl at various temperatures and concentrations of BPTU

<table>
<thead>
<tr>
<th>C (mol/L)</th>
<th>28°C</th>
<th>40°C</th>
<th>50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(E_{\text{corr}}) (mV)</td>
<td>(CR) (mpy)</td>
<td>(IE) (%)</td>
</tr>
<tr>
<td>Blank</td>
<td>-540</td>
<td>291.55</td>
<td>-</td>
</tr>
<tr>
<td>BPTU</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0001</td>
<td>-500</td>
<td>4.37</td>
<td>98.50</td>
</tr>
<tr>
<td>0.0002</td>
<td>-487</td>
<td>3.70</td>
<td>98.73</td>
</tr>
<tr>
<td>0.0003</td>
<td>-480</td>
<td>3.21</td>
<td>98.90</td>
</tr>
<tr>
<td>0.0004</td>
<td>-483</td>
<td>3.35</td>
<td>98.85</td>
</tr>
</tbody>
</table>

Table 3 Linear polarization results for low carbon steel in 0.1 M HCl at various temperatures and concentrations of BPTU

<table>
<thead>
<tr>
<th>C (mol/L)</th>
<th>28°C</th>
<th>40°C</th>
<th>50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(OCP) (mV)</td>
<td>(CR) (mpy)</td>
<td>(IE) (%)</td>
</tr>
<tr>
<td>Blank</td>
<td>-550</td>
<td>280.49</td>
<td>-</td>
</tr>
<tr>
<td>BPTU</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0001</td>
<td>-495</td>
<td>4.37</td>
<td>98.60</td>
</tr>
<tr>
<td>0.0002</td>
<td>-480</td>
<td>3.70</td>
<td>98.85</td>
</tr>
<tr>
<td>0.0003</td>
<td>-475</td>
<td>3.21</td>
<td>98.89</td>
</tr>
<tr>
<td>0.0004</td>
<td>-480</td>
<td>3.35</td>
<td>98.86</td>
</tr>
</tbody>
</table>

Figure 6 Tafel extrapolation curves for low carbon steel in 0.1 M HCl in the absence and presence of 0.0004 mol/L of BPTU at: (a) 28°C; (b) 40°C; and (c) 50°C
It is observed from the Figure 6 and Tables 2 and 3 so that the presence of BPTU drastically reduces the corrosion current and shifts the corrosion potential in the positive direction. The swing in corrosion potential ($E_{corr}$) in the positive path reveals that the BPTU predominantly acts as an anodic inhibitor for low carbon steel. The investigation illustrated that (Tables 2 and 3) indicate that the protective efficiency of the compound has a positive correlation with the concentration of BPTU accepted in 0.0004 mol/L. The upsurge in protective efficiency (IE) is up to the critical concentration (0.0003 mol/L), which may be owing to the stalling effect of the metal surface by both adsorption and the film formation mechanism, which reduces the active area of attack. Since the protective efficiency of BPTU is more than 97% in the range of temperatures studied, it can be effectively used as an inhibitor for preventing the anodic dissolution of metals in HCl media in industries. From the results, it can be seen that there is a marginal decrease in IE of the compound in the presence of 0.0004 mol/L of BPTU at all temperatures studied. This may be due to the desorption of inhibitor molecules from the metal surface. Excellent protective efficiency demonstrated by the compound may be due to its adsorption on the metal surface through polar groups as well as through π-electrons of the double bond. The investigation shows that IE of the compound deduced from the Tafel extrapolation and the linear polarization techniques were in good agreement.

The influence of temperature on protective efficiency is shown in Tables 2 and 3. From the tables, it can be seen that there is not much variation in the protective efficiency of BPTU in the range of temperatures studied. This reveals that the compound investigated was insensitive to the temperatures in the HCl medium and it also reveals that effectiveness of BPTU was not lost even at the elevated temperatures. Therefore, the compound investigated can be efficiently used as an inhibitor for mitigating the corrosion of low carbon steel at higher temperatures in an acid solution. Good performance demonstrated by BPTU may be due to the existence of the protonated form of N and S atoms of the compound which makes it adsorbed rapidly on the metal surface, thus forming an insoluble stable film on the surface of the mild steel. Since sulphur is less electronegative than nitrogen and has two electron pairs available for coordination, the bonding between the inhibitor molecule and the steel surface most likely occurs through a sulphur atom. The study also reveals that the corrosion rate increased substantially in line with the solution temperature in the absence of inhibitor. This is because the increase in solution temperature increases the anodic dissolution of metals (Riastutti et al., 2016).

The values of kinetic parameters for the adsorption of the inhibitor will give clear evidence about the mechanism of corrosion inhibition. The free energy of adsorption ($\Delta G_{ads}$), the equilibrium constant (K) and the activation energy ($E_a$) at various temperatures were estimated using the following Equations 5, 5.1, 5.2, and 6:

$$\Delta G_{ads} = -RT \ln(55.5K)$$  \hspace{1cm} (5)

where, $R$ is the universal gas constant in J/k/mol, $T$ is the temperature in Kelvin and 55.5 is the concentration of water in mol/L.

$$K = \theta / C(1-\theta)$$  \hspace{1cm} (5.1)

where, $\theta$ is the degree of surface coverage on the metal surface, $C$ is the concentration of inhibitor in mol/L.

$$C = \text{ppm} \times 10^{-3} / \text{mol.wt}$$  \hspace{1cm} (5.2)
where, ppm is parts per million, and mol. wt. is the molecular weight of the compound in grams/mol.

\[
\ln \left( \frac{r_2}{r_1} \right) = -\frac{E_a \Delta T}{R \times T_1 \times T_2}
\]  

(6)

where, \( r_1 \) and \( r_2 \) are the corrosion rates at temperatures \( T_1 \) and \( T_2 \) respectively and \( \Delta T \) is the difference in temperature \( (T_1 - T_2) \).

Table 4 Activation energy and free energy of adsorption for low carbon steel in 0.1 M HCl in the absence and presence of 0.0004 mol/L of BPTU

<table>
<thead>
<tr>
<th>System</th>
<th>( E_a ) (kJ/mol)</th>
<th>(-\Delta G_{ad}(kJ/mol))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M HCl</td>
<td>24.38</td>
<td>40°C</td>
</tr>
<tr>
<td>BPTU</td>
<td>52.96</td>
<td>40.70</td>
</tr>
</tbody>
</table>

The results of \( E_a \) and \( \Delta G_{ad} \) of the compound studied are given in Table 4. From Table 4, it is concluded that the values of \( \Delta G_{ad} \) of BPTU obtained at various temperatures were higher than 40 kJ/mol. This shows that the inhibition was steered by a chemisorption mechanism (Quraishi et al., 2002; Vishwanatham & Emranuzzaman, 1998). Chemisorption can also be confirmed from the influence of inhibitor concentrations on \( E_{corr} \) at different temperatures. The investigation shows that \( E_{corr} \) shifts in the positive direction with the existence of BPTU at different temperatures. This indicates that the suppression of the anodic reaction was due to the blocking of the anodic site by chemisorption of the electron rich N-S functionality to the positive centers of the metal (Ali et al., 2005). The negative values of \( \Delta G_{ad} \) were indicative of extemporaneous adsorption and a sturdy interface of inhibitor molecules with the low carbon steel surface (Shetty & Shetty, 2008). The greater value of \( E_a \) in the presence inhibitor demonstrates that the compound investigated was also highly effective at lower temperatures (Quraishi & Sharma, 2004).

The stages of adsorption of an inhibitor on the steel surface are shown in Figure 7. The adsorption behaviour of the inhibitor investigated is determined by the presence of a double bond with the S-atom, which is an adsorption centre and that of \( \pi \)-electrons. There may be on the metal surface cathodic and anodic sites providing centers for cathodic and anodic reactions. However, even in the absence of these, the adsorption of an inhibitor on the metallic surface will introduce a partial negative charge at the point of attraction (Figure 7a). At first forces involved may be weak electrostatic forces, but these may develop into stronger forces at the chemisorption stage with the residual negative charge on the iron atom at the centre of attraction becoming larger.

The S-atom possesses vacant d- orbitals of symmetry, which are compatible with some of the d-orbitals of the metal atoms. The \( \pi \)-electrons present can overlap with the sulphur d-orbital and forming a partial \( \pi \)-\( \pi \) bond (Figure 7b), decreasing the residual +ve charge of the sulphur atom and the -ve charge of the Fe atoms, with a partial formation of a further bond or at least strengthening of the original electrostatic bond. The intensity of the negative charge on the metal atom can be reduced, either by back donation to the sulphur atom (Figure 7b), or by redistribution or concentration of the charge into a conveniently placed site at some distance from the adsorbed molecule (cathodic site) (Figure 7c). However, both phenomena may take
place simultaneously (Donnelly et al., 1974). The stages of adsorption show that the stability of the adsorption bond depends on the \( \pi \)-electron density at its center.

![Diagram of adsorption stages](image)

Figure 7 Stages in the adsorption of an inhibitor on the Fe surface

Furthermore, to know the mechanism of inhibitor, the manner in which the organic compound gets adsorbed on the metal surface needs to be identified. The degree of surface coverage (\( \theta \)) values for different concentrations of BPTU in the acid medium were verified graphically by fitting it to various isotherms. A plot of \( \theta \) versus log C displays a linear relationship (Figure 8), signifying that the adsorption of BPTU on the low carbon steel surface obeys Temkin’s adsorption isotherm. The applicability of Temkin’s adsorption isotherm confirms the assumption of a monolayer adsorption on a uniform homogeneous metal surface with an interaction in the adsorption layer (Stoyanova et al., 1997; Pandian & Sethuraman, 2009).

![Graph of Temkin's adsorption isotherm](image)

Figure 8 Temkin’s adsorption isotherm plot for low carbon steel in 0.1 M HCl with BPTU at 28°C, 40°C and 50°C

The photographs of the low carbon steel sample corroded in a 0.1 M HCl medium at 28°C in the absence and presence of 0.0004 mol/L of BPTU are shown in Figures 9a and 9b. The main mechanism of corrosion in an acid media may be due to the anodic dissolution of metal, either at the grain boundaries or at the metal-media interface. From Figure 9a, corrosion occurs by pitting along with a uniform attack is noticed at the metal media interface. Pitting corrosion is a form of an extremely localized attack that results in holes on the metal surface. Uniform attack
Electrochemical Corrosion of Low Carbon Steel in a Hydrochloric Acid Medium

is the most common form of corrosion that proceeds uniformly over the entire exposed surface of the metal.

Figure 9 Photographs of low carbon steel surface exposed to corrosion: (a) 0.1 M HCl; and (b) with 0.0004 mol/L of BPTU at 28°C

From Figure 9b, it is clear that BPTU inhibits the corrosion of low carbon steel to a greater extent by forming a protective layer on the surface of the metal, thereby preventing the metal-media interface. Due to this interface, corrosion by pitting and the uniform attack on the surface of the metal was almost controlled by the presence of BPTU. Furthermore, Figure 9b confirms the accuracy of the results obtained from the polarization studies and it is also clear evidence for the effectiveness of BPTU in preventing anodic dissolution of metal in an acid medium.

5. CONCLUSION

Based on the experimental results, it was observed that BPTU is an outstanding anodic inhibitor for low carbon steel in a HCl solution. The study demonstrated that the protective efficiencies were insensitive to the range of temperatures studied. The adsorption of BPTU on the low carbon steel surface follows Temkin’s adsorption isotherm and inhibition was governed by chemisorption mechanism. Since the compound investigated gives the highest inhibition efficiency (more than 97%) even at a very low concentration of BPTU, it can be successfully used as an inhibitor for mitigating the corrosion of mild steel in a hydrochloric acid media at elevated temperatures in industry.

6. REFERENCES


Shetty, S.D., Shetty, P., Nayak, H.V.S., 2006. Inhibition of Mild Steel Corrosion in Acid Media
Electrochemical Corrosion of Low Carbon Steel in a Hydrochloric Acid Medium


