Inhibition of mild steel corrosion in acid media by N-benzyl-N′-phenyl thiourea

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The inhibition effect of N-benzyl-N′-phenyl thiourea (BPTU) on the corrosion of mild steel in 0.01 and 0.05 N HCl medium has been investigated by potentiostatic polarization technique. Results obtained reveal that BPTU is an efficient anodic inhibitor with greater than 94% of efficiency in the range of temperature studied. The adsorption of inhibitor on the mild steel surface obeys the Temkin’s adsorption isotherm and the inhibition is governed by chemisorption mechanism. The kinetic parameters of adsorption obtained reveal spontaneous adsorption and a strong interaction of the compound on the mild steel surface. The influences of the parameters like temperature, HCl concentration and inhibitor concentration on the corrosion of mild steel has also been investigated.

Keywords: Corrosion inhibition, Mild steel, Hydrochloric acid, Potentiostatic polarization technique, Adsorption, Activation energy

Mild steel is a very prominent material of construction and frequently comes in contact with aqueous solution, which may be acidic in nature, as a part of industrial process. The study of corrosion of mild steel in acid media is of both academic and industrial significance that has received considerable attention1. Acid solutions are widely used in industry, the most important fields of application being acid pickling, industrial acid cleaning, acid descaling, gas and oil well acidizing. Acids are also used in numerous manufacturing processes in different industries2,3.

Hydrochloric acid solution readily attacks mild steel. It is possible to reduce the corrosion rate to safe level by adding inhibitors. The addition of inhibitors to the acid media has been found to be cost-effective way of mitigating metallic corrosion under conditions of moderate acid concentration and temperature4. The effect of temperature on the inhibiting process is of great importance in industry. Effective inhibitors are expected to perform under a wide range of conditions. Most of the well-known acid inhibitors are compounds containing nitrogen, sulphur and oxygen atoms, which are capable of retarding metallic corrosion. As the thiourea molecule contains one sulphur and two nitrogen atoms, thiourea and its derivatives can function as potential corrosion inhibitors. While investigations have been carried out on inhibitor properties of thiourea and substituted thioureas5,6, due attention has not yet been paid to a systematic study of inhibiting action of thiourea derivatives.

Thiourea alone increases the corrosion rate of mild steel in 10% hydrochloric acid. However, in the presence of ferric and cupric ions, thiourea effectively retards the corrosion process2. Both S-diethyl thiourea and S-dibutyl thiourea have been found to accelerate the corrosion process of iron and mild steel in acid media at lower concentrations5. Thiourea derivatives such as o-, m- and p-tolyl thiourea were investigated as corrosion inhibitors for steel in 5.0 N hydrochloric acid, but they were not found to be very effective9. Allylpyridyl thiourea and phenylpyridyl thiourea retard the corrosion of mild steel in 1 N HCl by influencing both anodic and cathodic reactions10. In earlier studies, the use of N-cyclohexyl-N′-phenyl thiourea and N-furfuryl-N′-phenyl thiourea as effective inhibitors for mild steel in HCl medium11,12 have been reported.

Some of the other derivatives of thiourea, which have been investigated earlier, are allyl thiourea, tollyl thiourea, phenyl thiourea, di-orthotolyl thiourea, di-orthoxenyl thiourea, phenyl otoyl thiourea, di-N-butyli thiourea, N-butyl thiourea, di-isopropyl thiourea, di-methyl thiourea tetramethyl thiourea, di-phenyl thiourea and N-(2-mercaptophenyl)-N′-phenyl thiourea13.

This paper deals with the study of inhibiting effect of N-benzyl-N′-phenyl thiourea (BPTU) on the corrosion behaviour of mild steel in acid media at
three different temperatures and at four levels of inhibitor concentration by potentiostatic polarization technique. The choice of BPTU is based on the fact that substituents to thiourea increase further its electron density for adsorption on the metal surface; moreover it can be synthesized conveniently from relatively cheap raw materials.

**Experimental Procedure**

**Medium**

Analytical Reagent grade HCl (Merck) and double distilled water were used for preparing test solution of 0.01 N and 0.05 N HCl for all experiments.

**Specimen**

The mild steel sample of composition (wt %): C: 0.205; Si: 0.06; Mn: 0.55; S: 0.047; P: 0.039 and balance Fe was used in the present study. The specimen of 12 mm diameter and 10 mm length was polished successively with 1/0-5/0 grade emery papers, thoroughly cleaned with soap water, rinsed with distilled water and then with alcohol and dried in air. The sample was tightly fitted to one end of the Teflon holder, which exposes a polished surface area of 0.786 cm².

**Inhibitor**

The compound, N-benzyl-N′-phenyl thiourea was synthesized by following the standard procedure 14. The purity of the compound was checked by elemental analysis and melting point (158°C). The structure of the compound is shown in Fig. 1.

**Polarization studies**

By using a Wenking potentiostat and a three-electrode cell, the electrochemical studies were performed in a five-necked glass assembly containing 400 mL of the electrolyte at room temperature (28°C) with specified concentrations of the inhibitor (0, 25, 50, 75, 100 ppm) dissolved in it. Steady state open circuit potential (OCP) with respect to a saturated calomel electrode (SCE) was noted at the end of 25-30 min. Polarization studies were then made from −250 mV versus OCP to + 250 mV versus OCP with a scanning rate of 20 mV per min from the cathodic side. Experiments were repeated at 40 and 50°C. The temperature was accurately maintained within the limit of ±1°C. Tafel graphs of potential versus log i were plotted and corrosion current density (Icorr) and corrosion potential (Ecorr) were determined in the absence and presence of inhibitor. The results were also cross-checked by linear polarization technique.

**Results and Discussion**

The inhibition effects of BPTU on the corrosion of mild steel in 0.01 and 0.05 N hydrochloric acid solutions, studied by potentiostatic polarization technique at different temperatures are shown in Table 1. It can be seen from the polarization curves

![Fig. 1 — Structure of N-benzyl-N′-phenyl thiourea](image)

### Table 1 — Corrosion inhibition of mild steel by BPTU in 0.01 N and 0.05 N HCl at different temperatures

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>C (ppm)</th>
<th>0.01 N HCl</th>
<th>0.05 N HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ecorr (mV)</td>
<td>CR (mpy)</td>
</tr>
<tr>
<td>28</td>
<td>00</td>
<td>-598</td>
<td>61.71</td>
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<tr>
<td></td>
<td>25</td>
<td>-455</td>
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<td></td>
<td>50</td>
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<tr>
<td></td>
<td>75</td>
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<tr>
<td></td>
<td>100</td>
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<td>-604</td>
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(Fig. 2) and their fitted results that there is a large positive shift in the corrosion potential ($E_{corr}$) and a drastic reduction in corrosion current density ($I_{corr}$) and corrosion rate values. The shift in corrosion potential in the positive direction indicates that BPTU is an anodic inhibitor. The corrosion rate, the percentage inhibition efficiency ($%IE$) and surface coverage ($\theta$) were calculated by using the following relations,

$$\text{Corrosion rate (mpy)} = \frac{0.1288 \times I (\mu A/cm^2) \times \text{eq wt (g)}}{D (g/cm^3)}$$  \hspace{1cm} ... (1)

where $I$ is the current density, $D$ is the density of mild steel and eq. wt is the equivalent weight of mild steel and 0.1288 is the metric and time conversion factor.

$$% IE = \left[ \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \right] \times 100$$  \hspace{1cm} ... (2)

$$\theta = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}}$$  \hspace{1cm} ... (3)

It has been observed from the results that $IE$ of BPTU increases with increase in inhibitor concentration at all temperatures up to a critical concentration. The increase in efficiency may be due to the blocking effect of the surface by both adsorption and film formation mechanism, which decreases the effective area of corrosion attack. The results confirm that BPTU is an excellent corrosion inhibitor, which gives efficiency values as high as 94% in the range of temperature studied. The excellent performance exhibited by the compound may be due to the presence of protonated form of N and S atoms of the compound which makes it adsorbed quickly 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 co-ordination, the bonding between the inhibitor molecule and the mild steel surface probably occurs through a sulphur atom.

The effect of the temperature on $IE$ is shown in Table 1. It is observed that $%IE$ did not change significantly with the increase in temperature from 28 to 50°C. This indicates that BPTU is not temperature sensitive. The high $IE$ exhibited by BPTU may be attributed to its adsorption on the metal surface through polar groups as well as through $\pi$-electrons of the double bond. This leads to greater coverage of the metal surface by BPTU, thereby resulting in higher $IE$. It is also observed from the results that corrosion rate values for mild steel increases more rapidly with temperature and HCl concentration in the absence of inhibitor. The raise in temperature results in an increase in conductance of the aqueous medium and thereby increases the diffusion rate of hydrogen ions to the metal surface. Hence the corrosion progresses faster at higher temperatures. The increase in corrosion rate with increase in acid concentration is expected because the reaction rate will be faster in higher concentration of acid due to more number of collisions of reacting molecules.

It is also observed from Table 1 that $% IE$ of BPTU increases as the concentration of acid increases. This may be so because the inhibitor ionizes more readily.

![Fig. 2 — Potentiodynamic polarization curves for mild steel by BPTU at 28°C in (a) 0.01 N HCl and (b) 0.05 N HCl.](image-url)
under more acidic conditions and is more easily adsorbed on the metal surface, hence increasing the inhibition efficiency. The inhibiting effect of BPTU can be attributed to its parallel adsorption at the metal solution interface. The parallel adsorption takes place owing to the presence of one or more active centre for adsorption. The chemisorption takes place by the formation of a chemical bond between the metal and the adsorption molecules.

To understand the mechanism of corrosion inhibition, the adsorption behaviour of the organic adsorbates on the metal surface must be known. The surface coverage values for different concentrations of inhibitor from the acid were tested by fitting to various isotherms. The $\theta$ versus log$C$ plot (Fig. 3) for different concentrations of BPTU shows a straight line, indicating that the adsorption of BPTU on the mild steel surface followed Temkins’ adsorption isotherm. The applicability of Temkins’ isotherm verifies the assumption of mono-layer adsorption on a uniform, homogeneous metal surface with an interaction in the adsorption layer.

The bonding of adsorbed corrosion inhibitor molecule onto the metal surface can be described in terms of concepts of “hard-soft acids and bases” and electrosorption valency. Inhibitive efficiencies change with the nature of substituents in the inhibitor molecules as electron densities change at functional groups. Substituents increase the inhibitive efficiency probably because of stronger adsorption forces arising from increased electron density due to a nucleophilic or electrophilic substituents. The inhibitive efficiency is also related with steric factor.

The values of activation energy ($E_a$) were calculated using Arrhenius equation.

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

where $r_1$ and $r_2$ are corrosion rates at temperature $T_1$ and $T_2$ respectively, $\Delta T$ is the difference in temperature ($T_1-T_2$) and $R$ is the universal gas constant in Joules. The values of $E_a$ in the inhibited solution are found to be higher (Table 2) compared to that in the uninhibited one, indicating that dissolution of the metal is retarded. The higher values of $E_a$ in the presence of BPTU than in its absence also indicate that the BPTU retards the corrosion process at ordinary temperature and it serves as a good evidence for the chemisorption mechanism of the compound on the steel surface.

The enhancement of efficiency with increase in inhibitor concentration either could be due to higher activation energy or due to the increase in surface coverage by the inhibitor.

The free energy of adsorption ($\Delta G_{ads}$) and the equilibrium constant ($K$) at different temperatures were calculated from the following equations.

$$\Delta G_{ads} = -RT \ln (55.5K)$$

where 55.5 is the concentration of water in solution in moles L$^{-1}$ and $T$ is the temperature in kelvin.

$$K = \frac{\theta}{C (1-\theta)}$$

where $\theta$ is the degree of surface coverage on the metal surface and $C$ is the concentration of inhibitor in mol L$^{-1}$. The negative values of $\Delta G_{ads}$ indicated (Table 2) spontaneous adsorption of the inhibitor molecules on the surface of mild steel. The negative values of $\Delta G_{ads}$ also indicate a strong interaction of the inhibitor molecules on the mild steel surface. The $\Delta G_{ads}$ values for the optimal concentration (100 ppm) of BPTU at higher temperatures were greater than or
nearly equal to 40 kJ mol\(^{-1}\), indicating that inhibitor molecules on the mild steel surface are chemisorbed\(^{24}\).

**Conclusion**

From the results the following can be concluded that:

(i) BPTU is an efficient anodic inhibitor.
(ii) Polarization behaviour of mild steel in presence of BPTU showed drastic reduction in the corrosion rate.
(iii) The adsorption is spontaneous with a strong interaction of the compound on the mild steel surface.
(iv) The inhibition efficiency values are nearly constant in the range of temperature studied.
(v) The inhibition as high as 94% was obtained at different inhibitor concentrations studied.
(vi) BPTU forms a chemisorbed film on the mild steel surface following Temkins’ adsorption isotherm.
(vii) \(\%\) IE increases with increase in concentration of the hydrochloric acid medium.
(viii) The protective effect of BPTU is not lost even by increasing the temperature up to 50\(^\circ\)C.

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**References**