CHAPTER 12

ANTI-CORROSION STUDIES ON SOME THIOUREA DERIVATIVES

12.1 INTRODUCTION

Thiourea and its derivatives have been shown to exhibit good anticorrosion properties (Lawson 1980). With a view to establish the structure and activity relationship of the thiourea derivatives studied in the earlier chapters, some of these compounds were tested for anticorrosion properties. These results are presented in this chapter.

12.2 ANTI-CORROSION STUDIES

Inhibition is a preventive measure against corrosive attack on metallic materials which involves the use of a chemical compound which when added in small concentration to an aggressive environment reduces the aggressivity of the environment and thereby preventing the corrosion of the exposed metal (Riggs 1973). Out of the variegated classes of inhibitors, the organic adsorption type inhibitors are by far the best class of inhibitors, suitable for industrial environments. The inhibiting action exercised by organic compounds on the dissolution of metallic materials is normally attributed to interactions by adsorption between the inhibitor and the metal surface. The possibility of correlating structural characteristics with inhibitor properties of organic compounds is justified by the fact that the metal inhibitor interactions are based on chemisorption. The electron density of the organic functional group that can be defined as the reaction
center for the establishment of adsorption bond is then obviously important, since it is possible to assume a bond of Lewis acid-base type, generally with the inhibitor as the electron donor and the metal on the electron acceptor. The strength of this bond depends on the characteristics of both the adsorbent and the adsorbate (Trabanelli et al. 1970; Riggs 1973; Chandrasekarpillai 1975; Chandrasekarpillai et al. 1978 and Fontana 1987).

Most organic inhibitors are compounds with at least one polar functional group having atoms of nitrogen, sulphur, oxygen, selenium and phosphorous. In general, the polar group is regarded as the reaction center for the establishment of the chemisorption process. In such a case the adsorption bond strength is determined by the electron density of the atom acting as the reaction center and by the polarizibility of the functional group (Trabanelli et al. 1970; Riggs 1973 and Fontana 1987).

The idea of electron density acquires particular importance in the organic inhibitors whose structure may be affected by introduction of different substituents in different positions. The availability of electron pair for the formation of chemisorption bonds can thus be altered by regular and systematic variations of the molecular structure (Hoar et al. 1953). In view of the above facts that the known inhibitory action of the simple thiourea can be improved with inclusion of different substituents onto nitrogen atoms. Such derivatives are expected to yield better corrosion performance than the mere thiourea.

12.3 EXPERIMENTAL METHOD

Experiments were performed with mild steel specimen having the composition as listed in Table 12.1. For weightloss measurements rectangular specimens with a size of 2 x 5 x 1 cm were used. The specimens were uniformly polished with emery papers, washed with distilled water degreased with acetone and dried. Electrolyte used was 1.0M HCl
(uninhibited solution). Specimens were immersed in a 500 ml of the test solution as a blank and also with various concentrations of thiourea derivatives (inhibited solution) for 5 hours. The weightloss data were recorded. The experiments were carried out by weightloss method, because of its easy handling procedure.

12.4 RESULTS AND DISCUSSION

Immersion corrosion experiments for mild steel specimens in 1.0 M hydrochloric acid solution in the absence and presence of different types of inhibitors viz., TU (thiourea), APTU, CHPTU, CHTTU, DMTTU, DBTU, DPTU and OCDPTU were carried out over a period of 5 hours. The corrosion of the specimens reaching a constant value at a certain concentration of a thiourea derivative is called critical inhibitor concentration. In the presence of thiourea the corrosion rate was progressively decreased with increase in concentration upto 5.0 mM. The percentage of inhibitor efficiency is calculated from the following equation

\[ I = \left(\frac{W_b - W_i}{W_b}\right) \times 100\% \quad \text{(12.1)} \]

where

- \( I \) = the inhibition efficiency
- \( W_b \) = Weight loss observed with uninhibited solution
- \( W_i \) = Weight loss observed with inhibited solution

The effect of critical inhibitor concentration of thiourea and its derivatives over the mild steel in 1.0 M HCl was shown in Table 12.2.

From the data in the Table 12.2, it is inferred that the inhibition efficiency of the thiourea derivatives are remarkably higher than the simple thiourea alone. Hence, the observed higher inhibition efficiency can be
correlated with the nature of the substituents present in the thiourea molecule, which somehow influences the thiourea molecule to act better. The action may be through the electron density or steric effect or both the effects.

Both electron density and shielding (steric) effects play an important role in determining the corrosion rates of various substituted thiourea molecules. Trabanelli et al (1973) have pointed out the importance of these two effects by increasing electron density at the sulfur atom in mercaptans and sulfides increases the inhibition efficiency. The inhibition arises due to the ability of these compounds to chemisorb at the metal surface by virtue of their lone electron pairs. They have suggested that the electronic charge on sulfur atom is an important factor but it cannot explain all the observed facts. The inhibition efficiency can also be attributed to the steric effect or the screening action of the hydrocarbon chains. The observed dependence of inhibition efficiency with the thiourea derivatives under investigation can be readily explained on the basis of the above discussion. When these compounds are present in small concentration (0.1 to 0.5 mM level) the adsorbed layer is incomplete and the dissolution is only partially inhibited. Moreover, the hydrogen sulfide produced by the cathodic reduction of the thiourea derivatives accelerates the dissolution. Hence, the overall result is acceleration. However, at higher concentrations of the thiourea derivatives, the adsorption becomes extensive enough to decrease the rate of anodic reaction considerably and consequently the cathodic reaction rate is also decreased. Hydrogen sulfide is still produced, but its accelerating effect is considerably less pronounced as the metal surface is more or less completely covered.

Inhibition of mild steel corrosion results under these conditions. When a particular derivative is not extensively adsorbed, which apparently is the case with thiourea itself, acceleration becomes more pronounced as the concentration is increased, because of the greater amount of hydrogen
sulfide produced. However, the extent of adsorption is enhanced through the substitution of organic groups on thiourea, which consequently changes the solubility, electronic structure of the functional groups and structure of the adsorbed film (Trabanelli et al 1970).

Adsorption (Chemisorption) is more or less reversible and consequently the extent of chemisorption of these compounds should be a function of their solubility. Thus the thiourea derivatives studied viz., TU, ALPTU, CHPTU, CHTTU, DMTTU, DBTU, DPTU and OCDPTU, the inhibition efficiency increases as the solubility decreases. The order of inhibition efficiency is OCDPTU > DPTU > DBTU > DMTTU > CHTTU > CHPTU > ALPTU > TU.

These thiourea derivatives can be divided into two groups based on their inhibition efficiency. OCDPTU, DPTU and DBTU form group A, with inhibition efficiency ranging from 87-90%. The inhibition efficiency of the other group, group B which comprises of DMTTU, CHTTU, CHPTU and ALPTU range from 62-65%. Changes in the electron density of the sulfur and nitrogen is caused by the substitution of organic groups to the thiourea molecule. The increase in the electron density around sulfur and nitrogen enhanced the chemisorption of these compounds over the mild steel surface. In the present investigation, the chemisorption could be more favoured for group A compounds, since the electron density around N and S will be high besides the presence of delocalized electron clouds around two phenyl groups, which also contributes to the adsorption phenomena.

Moreover, the geometrical factors also determine the closeness of the packing in the adsorbed film. The X-ray crystal structure determination studies reveal, N-H...S hydrogen bonds stabilised the solid state packing for group A compounds, whereas in group B compounds this lacks. During the surface film formation the same closeness in the packing may be expected for these compounds.
On the basis of the facts availed from the above study, it can be concluded that the thiourea derivatives are better corrosion inhibitors for mild steel in acidic solutions than the thiourea alone. The enhanced inhibitory action exerted by these derivatives can be attributed to the substituents present in the thiourea molecule. These substituents influence the inhibitory action of molecules by decreasing the solubility and increasing the chemisorption through the delocalized electron clouds around the phenyl ring besides providing better surface coverage.
### TABLE 12.1

Chemical composition of mild steel specimen (wt %)

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.47</td>
<td>0.089</td>
<td>0.049</td>
<td>0.042</td>
<td>Balance</td>
</tr>
</tbody>
</table>

### Table 12.2

Percentage inhibition efficiency of thiourea and its derivatives over mild steel in 1.0M HCl

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Experiment</th>
<th>Wt. loss (mg/cm/hour)</th>
<th>Inhibition Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Blank (1.0M HCl)</td>
<td>5.1260</td>
<td>—</td>
</tr>
<tr>
<td>2.</td>
<td>Thiourea (5.0mM)</td>
<td>2.3256</td>
<td>54.63</td>
</tr>
<tr>
<td>3.</td>
<td>ALPTU (5.0mM)</td>
<td>1.9278</td>
<td>62.39</td>
</tr>
<tr>
<td>4.</td>
<td>CHPTU (5.0mM)</td>
<td>1.9012</td>
<td>62.91</td>
</tr>
<tr>
<td>5.</td>
<td>CHTTU (5.0mM)</td>
<td>1.8525</td>
<td>63.86</td>
</tr>
<tr>
<td>6.</td>
<td>DMTTU (5.0mM)</td>
<td>1.8274</td>
<td>64.35</td>
</tr>
<tr>
<td>7.</td>
<td>DBTU (4.0mM)</td>
<td>0.6319</td>
<td>87.67</td>
</tr>
<tr>
<td>8.</td>
<td>DPTU (4.0mM)</td>
<td>0.5817</td>
<td>88.65</td>
</tr>
<tr>
<td>9.</td>
<td>OCDPTU (4.0mM)</td>
<td>0.5218</td>
<td>89.82</td>
</tr>
</tbody>
</table>