Substituted thiobiurets and their molybdenum and tungsten complexes as corrosion inhibitors for mild steel in 1.0 N sulphuric acid

R B Rastogi, M M Singh, M Yadav & K Singh

Department of Applied Chemistry, Institute of Technology, Banaras Hindu University, Varanasi 221 005, India

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Corrosion inhibition studies of mild steel in 1.0 N sulphuric acid have been performed at 25°C using substituted thiobiurets and their molybdenum and tungsten complexes as inhibitors. All the inhibitors have been found to inhibit the corrosion process by getting adsorbed on the metal surface. Among the studied thiobiurets, methoxyphenyl derivative behaved as the best corrosion inhibitor. The inhibitive properties of thiobiurets improved considerably on complexation with molybdenum and/or tungsten ions.

Organic compounds either long chain or heterocyclic containing nitrogen, sulphur and oxygen have been frequently used as corrosion inhibitors for a number of metals and their alloys in a variety of environments. Heterocyclic compounds containing nitrogen, sulphur and oxygen atoms have been used as good inhibitors. These compounds inhibit corrosion due to presence of multiple active centres for adsorption and their efficiency depends upon number of active centres and relative surface area. Among inorganic compounds benzoates, nitrites, chromates and phosphates are some of the good inhibitors.

Recently, metal complexes have attained a prominent place as corrosion inhibitors because of their high efficiency even with small dosage. Mild steel is considered as an inexpensive structural material particularly for construction of storage tanks and pipe lines. It is susceptible to attack by sulphuric acid during operations like cleaning, pickling, descaling, transportation and acidizing in mining and oil wells. Thus, it was considered worthwhile to study the inhibitive properties of a few thiobiurets and their molybdenum and tungsten complexes for mild steel-1.0 N sulphuric acid system.

Experimental Procedure

The working electrode and specimens for weight loss experiments were prepared from mild steel sheets having the following percentage composition:

| Element | C | Mn | Si | P | S | N | Cu | Cr | Fe
|---------|---|----|----|---|---|---|----|----|---
|         | 0.12 | 0.11 | 0.02 | 0.02 | 0.02 | 0.01 | 0.01 |

The specimens for the weight loss experiments were of the size 3 cm x 3 cm and those for electrochemical studies the size of the electrodes was 1 cm x 1 cm with a 4 cm long tag for electrochemical contact. Both sides of the specimens were exposed for both techniques. The specimens were mechanically polished successively with 1/0, 2/0, 3/0 and 4/0 grade emery papers. After polishing with the paper of each grade, the surface was thoroughly washed with soap, running tap water, distilled water and finally was degreased with acetone. The samples were dried and stored in a vacuum desiccator before immersing in the test solution. For weight loss experiments 300 mL of 1.0 N H₂SO₄ was taken in 500 mL glass beakers with lids. The inhibition efficiencies were evaluated after 24 h using 10, 20, 50, 100 and 150 ppm of inhibitors. The specimens were removed from the electrolyte, washed thoroughly with distilled water, dried and weighed.

The electrochemical experiments were carried out in a three-necked glass assembly containing 150 mL of the electrolyte with different concentrations of inhibitors (from 10 ppm to 150 ppm by weight) in it. Polarisation studies were performed in un-stirred and non-deaerated solutions using a Wenking potentiostat (POS-73). Starting from open circuit potential, the potential was manually applied in 10 mV steps in the anodic or cathodic direction and the corresponding steady state currents were measured directly from the ammeter on the panel of potentiostat. All experiments were performed at 25 ± 0.2°C in an electronically controlled air thermostat.

The substituted thiobiurets were prepared by the method reported earlier. The metal complexes of these ligands were prepared by mixing an acidified aqueous solution of sodium molybdate/tungstate and...
an ethanolic solution of the corresponding ligand in 1:1 molar ratio. After digesting the reaction mixture on water bath, the precipitate obtained was filtered, washed with hot water followed by ethanol and dried in vacuo.

Results and Discussion

The percentage inhibition efficiency (IE) in the presence of 10, 20, 50, 100 and 150 ppm of all the inhibitors for corrosion of mild steel in 1.0 N H₂SO₄ solution at 25°C has been determined by weight loss and electrochemical techniques and the results are summarized in Table I. The structures of different inhibitors are given below:

\[ R - \text{NH} - C - \text{NH} - C - \text{NH} - \text{O} \]

\[ R = C₆H₅, -p-\text{CH₃}C₆H₄, -p-\text{CH₂O}C₆H₄, -p-\text{Cl}C₆H₄. \]

(I) (II) (III) (IV)

Organic inhibitors

\[ M=\text{Molybdenum} \]
\[ R = C₆H₅, -p-\text{CH₃}C₆H₄, -p-\text{CH₂O}C₆H₄, -p-\text{Cl}C₆H₄. \]

(V) (VI) (VII) (VIII)

M=Tungsten

\[ R = C₆H₅, -p-\text{CH₃}C₆H₄, -p-\text{CH₂O}C₆H₄, -p-\text{Cl}C₆H₄. \]

(IX) (X) (XI) (XII)

Metal complexes as inhibitors

It may be noted from Table I that IE in general increases with increase in concentration of the additives. On the basis of inhibition efficiency determined at all the experimental concentrations, studied following order emerges:

III > II > I > IV

An overview of the structure of thioureas indicates that the probable sites through which adsorption could occur, appear to be S, O and phenyl ring. The involvement of phenyl ring in adsorption is evident by enhanced IE in case of methoxy and methyl substituents due to their +I effect and reduced IE in case of chloro substituent on part of its -I effect.

The inhibition properties exhibited by the molybdenum and tungsten complexes are exactly in the same order as their respective ligands.

VII > VI > V > VIII and XI > X > IX > XII

In addition to this, the data recorded in the table show that molybdenum and tungsten complexes exhibit higher %IE than the corresponding ligands which may be attributed to their larger surface area and larger number of active centres of adsorption. Further, molybdenum and tungsten complexes of the same ligand do not differ much in their %IE values as both have the similar structures. Thus, it may be interpreted that the presence of metal atoms results in

![Fig. 1—Anodic polarization behaviour of mild steel in 1N sulphuric acid in absence and presence of different concentrations of Inh-1 (\(\rightarrow\) Blank; - - 20 ppm; \(\Delta\) - 50 ppm; \(\times\) 100 ppm; \(\bullet\) - 150 ppm)](image-url)
Table 1—Percentage inhibition efficiency (% IE) values calculated by weight loss and polarisation techniques in presence of different thiobiurets and their Mo(V) and W(V) complexes

<table>
<thead>
<tr>
<th>Concentration ppm</th>
<th>Ligand</th>
<th>Mo(V) Complex</th>
<th>W(V) Complex</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight loss method</td>
<td>Polarisation method</td>
<td>Weight loss method</td>
</tr>
<tr>
<td>1,5-diphenyl-2-thiobiuret</td>
<td></td>
<td></td>
<td>1,5-diphenyl-2-thiobiuret</td>
</tr>
<tr>
<td>10</td>
<td>66.31</td>
<td>65.12</td>
<td>74.21</td>
</tr>
<tr>
<td>20</td>
<td>72.24</td>
<td>70.86</td>
<td>84.34</td>
</tr>
<tr>
<td>50</td>
<td>76.12</td>
<td>75.16</td>
<td>89.34</td>
</tr>
<tr>
<td>100</td>
<td>81.31</td>
<td>80.12</td>
<td>93.16</td>
</tr>
<tr>
<td>150</td>
<td>83.12</td>
<td>81.93</td>
<td>94.21</td>
</tr>
<tr>
<td>1-p-methoxyphenyl-5-phenyl-2-thiobiuret</td>
<td></td>
<td></td>
<td>1-p-methoxyphenyl-5-phenyl-2-thiobiuret</td>
</tr>
<tr>
<td>10</td>
<td>66.18</td>
<td>66.34</td>
<td>78.12</td>
</tr>
<tr>
<td>20</td>
<td>72.24</td>
<td>70.86</td>
<td>84.34</td>
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<tr>
<td>150</td>
<td>83.12</td>
<td>81.93</td>
<td>94.21</td>
</tr>
<tr>
<td>1-p-chlorophenyl-5-phenyl-2-thiobiuret</td>
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<td>1-p-chlorophenyl-5-phenyl-2-thiobiuret</td>
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<td>150</td>
<td>83.12</td>
<td>81.93</td>
<td>94.21</td>
</tr>
</tbody>
</table>

An increase in the projected surface area and number of active sites thereby increasing %IE but overall mechanism of inhibition remains unaffected.

The anodic polarization behaviour of mild steel was studied in 1.0 N sulphuric acid containing different concentrations of substituted thiobiurets and their molybdenum and tungsten complexes at 25°C. Fig. 1 represents the anodic polarization behaviour of mild steel in presence of 20, 50, 100 and 150 ppm of 1,5-diphenyl-2-thiobiuret. It is evident from the figure that current density decreases with increase in concentration of the additive and the curves shift simultaneously towards noble direction. The magnitude of the shift in the anodic polarization curve is a function of the concentration of the inhibitors and their inhibition efficiencies at the respective concentrations.

The curves in the Fig. 2 illustrate the anodic polarization behaviour of mild steel in absence and presence of different concentrations of 1,5-diphenyl-2-thiobiuret complex of molybdenum at 25°C. The nature of the polarization curves both with and without inhibitors is almost identical showing a gradual shift in the polarization curves towards lower current density region with increase in the concentration of the additive. Thus the inhibitor may be considered to inhibit the corrosion of mild steel by blanketing the electrode surface without any interference with the anodic process.

Anodic polarization behaviour in the presence of tungsten complexes of all the ligands at their different concentrations has been studied at 25°C. However, the anodic polarization behaviour of mild steel in 1.0 N sulphuric acid containing 20 and 150 ppm only of methoxy-substituted derivative of 1,5-diphenyl-2-thiobiuret and its molybdenum and tungsten complexes are being shown in Fig. 3. It is observed from the figure that the difference between the shifts for molybdenum and tungsten is appreciable in case of 20 ppm concentration but it is negligible at 150 ppm concentration and it is in accordance with the inhibition efficiencies calculated by the weight loss technique.
Fig. 2—Anodic polarization behaviour of mild steel in 1N sulphuric acid in absence and presence of different concentrations of Inh-V (○—Blank; ■—20 ppm; ▲—50 ppm; ▲—100 ppm; ×—150 ppm)

Fig. 3—Anodic polarization behaviour of mild steel in 1N sulphuric acid in absence and presence of 20 and 150 ppm of Inh-III, VII, XI (○—Blank; ■—20 ppm of Inh-III; ▲—20 ppm of Inh-VII; ×—20 ppm of Inh-XI; ×—150 ppm of Inh-III; ●—150 ppm of Inh-VII; ×—150 ppm of Inh-XI)

Fig. 4—Cathodic polarization behaviour of mild steel in 1N sulphuric acid in absence and presence of different concentrations of Inh-II (○—Blank; ■—20 ppm; ▲—50 ppm; ×—100 ppm; ×—150 ppm)

Fig. 5—Cathodic polarization behaviour of mild steel in 1N sulphuric acid in absence and presence of different concentrations of Inh-V (○—Blank; ■—20 ppm; ▲—50 ppm; ×—100 ppm; ×—150 ppm)
Fig. 6—Cathodic polarization behaviour of mild steel in 1N sulphuric acid in absence and presence of 20 and 150 ppm of Inh-III, VII, XI (— Blank; — 20 ppm of Inh-III; — Δ — 20 ppm of Inh-VII; — x — 20 ppm of Inh-XI; — × 150 ppm of Inh-III; — o — 150 ppm of Inh-VII; — – — 150 ppm of Inh-XI

Fig. 7—Langmuir plots (— 0— Inh-I; — o — Inh-II; — Δ — Inh-III; — o — Inh-IV; — × — Inh-V; — x — Inh-VI; — Δ — Inh-VII; — o — Inh-VIII; — — Inh-IX; — — Inh-X; — Δ — Inh-XI; — — Inh-XII)

Fig. 8—Temkin plots (— 0— Inh-I; — o — Inh-II; — Δ — Inh-III; — o — Inh-IV; — × — Inh-V; — x — Inh-VI; — Δ — Inh-VII; — o — Inh-VIII; — — Inh-IX; — — Inh-X; — Δ — Inh-XI; — — Inh-XII)

Figs 4 and 5 represent the cathodic polarization behaviour of mild steel in absence and presence of different concentrations of 1,5-diphenyl-2-thiobuaret and its molybdenum complex respectively in 1.0 N sulphuric acid at 25°C. It is apparent from the figures that the nature of the curve remains almost unaltered on the addition of the inhibitors, however, some decrease in current density is observed on the addition of each of the inhibitors. The magnitude of the decrease in current density varied according to the nature of the inhibitor, it is in the same order as the IE obtained for these inhibitors from the weight loss and electrochemical techniques.

Fig. 6 represents the cathodic polarization behaviour of mild steel in 1.0 N sulphuric acid in presence and absence of 20 and 150 ppm of 1-p-methoxyphenyl-5-phenyl-2-thiobuaret and its molybdenum and tungsten complexes. It is again evident from the figure that the shift towards lower current density in case of molybdenum and tungsten complexes both affect the anodic as well as the cathodic current density by approximately the same extent at 150 ppm. It is also inferred from the figure that the shift in case of tungsten complexes is
substituted thiobiurets methoxy phenyl derivative exhibited the best corrosion inhibition properties. The complexation of a thiobiuret resulted in enhanced IE. Tungsten complexes proved to be better inhibitors than their molybdenum analogues at lower concentrations, however, at higher concentrations both are almost equally effective.

References