INHIBITION OF CORROSION OF CARBON STEEL IN SEA WATER BY THIOMALIC ACID - Zn²⁺ SYSTEM

S. K. Selvaraj[a], A. John Amalraj[b]*, V. Dharmalingam[b], J. Wilson Sahayaraj[c]

[a] PG and Research Department of Chemistry, G.T.N Arts. College, Dindigul - 624005, Tamil Nadu, India.
[b] PG and Research Department of Chemistry, Periyar E.V.R College (A), Tiruchirappalli - 620023, Tamil Nadu, India.
[c] Department of Chemistry, Jepiar Engineering College, Chennai- 600019, Tamil Nadu, India.

ABSTRACT

The synergistic effect has been studied in the presence of a dicarboxylic acid inhibitor with or without bivalent cation like zinc ions. A protective film has been formed on the carbon steel surface in aqueous solution using a synergistic combination of an environmentally friendly dicarboxylic acid (thiomalic acid) and zinc ions. The corrosion inhibition effect of thiomalic acid with zinc ions on carbon steel has been carried out by weightloss studies and electrochemical techniques. Potentiodynamic polarization studies reveal that the inhibitor system is of an anodic type. Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were used to investigate the nature of protective film formed on the carbon steel surface and for explaining the mechanistic aspects of the inhibition process.

Keywords: Thiomalic acid, corrosion inhibition, carbon steel, FT-IR and SEM.
1. INTRODUCTION

Because of its good mechanical properties, availability and relatively reasonable cost carbon steel is the most worldwide used material for industrial and domestic applications. Several techniques have been applied in order to reduce the corrosion of metals. The use of inhibitors was one of the most practical and efficient methods for protection against corrosion\cite{1}. Corrosion inhibitors are substances added in very small concentrations that they effectively reduce the corrosion rate\cite{2}. Generally, organic compounds having heteroatom O, N, P and S are found to have basicity and electron density, thus assist in corrosion inhibition\cite{3}. Compounds with functional groups containing hetero-atoms which can donate a lone pair of electrons are found to be useful as corrosion inhibitors for metals\cite{4-5}. These compounds are still continuously investigated as inhibitors for corrosion of metals in industry. The selection criteria for various inhibitors include low concentration, more adherence to environmental regulations, environmental friendliness and cost effectiveness. Carboxylic and dicarboxylic acids and salts thereof are very widely used as corrosion inhibiting agents and has been the subject of various workers\cite{6}. An inexpensive way to protect the metals from corrosion is by using carboxylic acids. Carboxylic acid derivatives alone or both with other additives can effectively inhibit the corrosion of metals. One of the most important effects in inhibition process that serves as the basis for most of the modern corrosion inhibiting formulations is synergism\cite{7}. Synergistic effect existing among dicarboxylic acids and Zn$^{2+}$ on the inhibition of corrosion of metals has been studied by various workers\cite{8-9}.

An organic compound namely dicarboxylic acid was investigated as a corrosion inhibitor for carbon steel in this study. The inhibitive properties and synergistic effect with an organic compound viz., Thiomalic acid (TMA) and Zn$^{2+}$ ions in controlling the corrosion of carbon steel was studied in sea water using weightloss method and electrochemical methods viz., potentiodynamic polarization. Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM) were used to analyse the protective film formed on the carbon steel surface and a suitable mechanism of corrosion inhibition is proposed\cite{10-14}.
2. EXPERIMENTAL

2.1. Preparation of Specimen

Carbon steel (0.026% S, 0.06% P, 0.4% Mn, 0.1% C, and the rest Fe) specimen of dimension 1cm × 4cm × 0.2cm were used for weight loss study. Carbon steel rod of the same composition, encapsulated in Teflon was polished to a mirror finish and degreased with trichloroethylene. Preparation of Stock solution is given in Table 1.

Table 1: Preparation of Stock Solution

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>CTAB Solution</th>
<th>Thiomalic acid (TMA)</th>
<th>ZnSO₄ solution</th>
<th>Total Volume made up with distilled water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ml ppm</td>
<td>ml ppm</td>
<td>ml Zn²⁺ (ppm)</td>
<td>ml</td>
</tr>
<tr>
<td>1.</td>
<td>1 100</td>
<td>0.5 50</td>
<td>1 10</td>
<td>100</td>
</tr>
<tr>
<td>2.</td>
<td>2 200</td>
<td>1 100</td>
<td>5 50</td>
<td>100</td>
</tr>
<tr>
<td>3.</td>
<td>3 300</td>
<td>2 200</td>
<td>10 100</td>
<td>100</td>
</tr>
<tr>
<td>4.</td>
<td>4 400</td>
<td>3 300</td>
<td>15 150</td>
<td>100</td>
</tr>
<tr>
<td>5.</td>
<td>5 500</td>
<td>4 400</td>
<td>20 200</td>
<td>-</td>
</tr>
</tbody>
</table>

2.2 Preparation of Thiomalic acid

1g of Thiomalic acid (TMA) was dissolved in distilled water and made up to 100 ml.

Figure 1. Structure of Thiomalic acid

2.3. Weight-Loss Method
Inhibition of corrosion ... thiomalic acid - Zn\(^{2+}\) system

Two carbon steel specimens were immersed in 100 ml of test solution containing various concentrations of the inhibitors in the absence and presence of Zn\(^{2+}\) ions, for a period of three days. After exposure corrosion product were removed with Clarke’s solution, and the weight of the specimens before and after immersion were determined using a metler balance.

2.4. Corrosion Inhibition Efficiency

Corrosion inhibition efficiency was calculated using the equation:

\[
I.E = 100 \left[ 1 - \frac{W_2}{W_1} \right] \%
\]

where

- \(W_1\): Corrosion rate in the absence of inhibitor,
- \(W_2\): Corrosion rate in the presence of inhibitor.

2.5. Surface Examination

The carbon steel specimens were immersed in various test solutions for a period of one day, taken out and dried. The nature of the film formed on the surface of metal specimens was analysed by FTIR spectroscopic study.

2.6. FT-IR Spectra

FT-IR spectra were recorded in a Perkin – Elmer 1600 spectrophotometer. The film was carefully removed, mixed thoroughly with KBr made in to pellets and FTIR spectra were recorded.

2.7. Potentiodyanmic Polarization

Polarization studies were carried out in an H&CH electrochemical work station impedance analyser model CHI 660A. a three electrode cell assembly was used. The working electrode was carbon steel. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode.

3. RESULTS AND DISCUSSION

3.1. Weight Loss Study

The corrosion rates of carbon steel immersed in various test solution for a period of one day are presented in the table 2.

Synergistic Effect of Thiomalic Acid – Zn\(^{2+}\) System
Table 2 Inhibition Efficiencies (IE%) and corrosion rates (CR) Obtained from TMA-Zn\(^{2+}\) systems when carbon steel immersed in Sea water.

Inhibitor system: TMA-Zn\(^{2+}\) Immersion period: 1 day

<table>
<thead>
<tr>
<th>TMA (ppm)</th>
<th>Zn(^{2+}) = 0 ppm</th>
<th>Zn(^{2+}) = 25 ppm</th>
<th>Zn(^{2+}) = 50 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IE%</td>
<td>CR (mmpy)</td>
<td>IE%</td>
</tr>
<tr>
<td>0</td>
<td>-</td>
<td>0.1136</td>
<td>18</td>
</tr>
<tr>
<td>50</td>
<td>13</td>
<td>0.0987</td>
<td>57</td>
</tr>
<tr>
<td>100</td>
<td>15</td>
<td>0.0964</td>
<td>68</td>
</tr>
<tr>
<td>150</td>
<td>17</td>
<td>0.0933</td>
<td>74</td>
</tr>
<tr>
<td>200</td>
<td>26</td>
<td>0.0836</td>
<td>78</td>
</tr>
<tr>
<td>250</td>
<td>33</td>
<td>0.0762</td>
<td>80</td>
</tr>
</tbody>
</table>

The calculated inhibition efficiencies of carbon steel immersed in Sea water, for a period of one day in the absence and presence of Zn\(^{2+}\) ion are given in table 2. The calculated value indicates the ability of TMA to be a good corrosion inhibitor. The IE is found to be enhanced in the presence of Zn\(^{2+}\) ion. TMA alone shows some IE. But the combination of 250 ppm TMA and 50 ppm Zn\(^{2+}\) shows 96% IE. This suggests a synergistic effect exists between TMA and Zn\(^{2+}\)[15-16].

Influence of Immersion Period on IE of TMA-Zn\(^{2+}\) System

Table 3 Influence of immersion period (IP) on IE of TMA (250ppm) - Zn\(^{2+}\) (50ppm) system

<table>
<thead>
<tr>
<th>System</th>
<th>Immersion period (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Sea water CR (mmpy)</td>
<td>0.1030</td>
</tr>
<tr>
<td>Sea water + TMA(250ppm)+ Zn(^{2+})(50ppm); CR (mmpy)</td>
<td>0.0035</td>
</tr>
<tr>
<td>IE %</td>
<td>96</td>
</tr>
</tbody>
</table>
The influence of immersion period on the IE of TMA (250ppm) – Zn\(^{2+}\) (50ppm) system is given in table 3 is found that as the IP increases, the IE decreases. This due to the fact as the IP increases the protective film formed on the metal surface is unable to withstand the continuous attack of corrosive ions such as chloride present in Sea water. There is a competition between two processes, namely, formation of FeCl\(_2\) (and also FeCl\(_2\)) and Fe\(^{2+}\)-TMA complex on the anodic sites of the metal surface. It appears that the formation of iron chlorides is more favoured than the formation of Fe\(^{2+}\)-TMA complex film formed on the metal surface is converted into iron chlorides which go into solution and hence, the IE decreases as the IP increases.

Influence of N-cetyl-N,N,N-trimethyl ammonium bromide(CTAB) on Inhibition Efficiency of TMA-Zn\(^{2+}\) System

**Table 4** Influence of CTAB on inhibition efficiency (IE\%) of carbon steel immersed in Sea water

<table>
<thead>
<tr>
<th>TMA Ppm</th>
<th>Zn(^{2+}) ppm</th>
<th>CTAB ppm</th>
<th>CR mmpy</th>
<th>IE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.1136</td>
<td>-</td>
</tr>
<tr>
<td>250</td>
<td>0</td>
<td>0</td>
<td>0.0045</td>
<td>94</td>
</tr>
<tr>
<td>250</td>
<td>50</td>
<td>0</td>
<td>0.0035</td>
<td>96</td>
</tr>
<tr>
<td>250</td>
<td>50</td>
<td>50</td>
<td>0.0035</td>
<td>96</td>
</tr>
<tr>
<td>250</td>
<td>50</td>
<td>100</td>
<td>0.0035</td>
<td>96</td>
</tr>
<tr>
<td>250</td>
<td>50</td>
<td>150</td>
<td>0.0033</td>
<td>100</td>
</tr>
<tr>
<td>250</td>
<td>50</td>
<td>200</td>
<td>0.0031</td>
<td>100</td>
</tr>
<tr>
<td>250</td>
<td>50</td>
<td>250</td>
<td>0.0032</td>
<td>100</td>
</tr>
</tbody>
</table>

CTAB is a cationic surfactant. It is a biocide. The IE and biocidal efficiency (BE) of TMA-Zn\(^{2+}\) CTAB system is given here it is observed from the results that 50 ppm of CTAB in combination with TMA-Zn\(^{2+}\) system has increased IE from 94\% to 96\%. However, a decrease in IE of TMA-Zn\(^{2+}\) System is noticed when the CTAB concentration increases from 100 ppm to 250 ppm. This is due to the formation of micelles at higher concentration of surfactant.

**3.2. Analysis of Polarization Curves for TMA-Zn\(^{2+}\) System**

**Table 5** The potentiodynamic polarization curves of carbon steel immersed in sea water in the absence and presence of inhibitor system obtained from potentiodynamic polarization study.
Inhibition of corrosion ... thiomalic acid - Zn\(^{2+}\) system

SK Selvaraj et al.,

<table>
<thead>
<tr>
<th>Description</th>
<th>(E_{\text{corr}}) mV/decade</th>
<th>(b_a) mV/decade</th>
<th>(b_c) mV/decade</th>
<th>LPR ohm cm(^2)</th>
<th>(I_{\text{corr}}) A/cm(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sea Water</td>
<td>-962</td>
<td>156</td>
<td>253</td>
<td>1.070 x 10(^5)</td>
<td>1.561 x 10(^{-4})</td>
</tr>
<tr>
<td>Sea Water + 50 ppm Zn(^{2+}) + 250 ppm TMA</td>
<td>-630</td>
<td>961</td>
<td>953</td>
<td>1.514 x 10(^6)</td>
<td>7.481 x 10(^{-6})</td>
</tr>
</tbody>
</table>

Fig. 2. Potentiodynamic polarization curves of carbon steel in various test solution

a) Sea Water  b) Sea Water + 50 ppm Zn\(^{2+}\) + 250 ppm TMA

The calculated corrosion parameters such as corrosion potential (\(E_{\text{corr}}\)), Tafel slopes (anodic slope \(b_a\) and cathodic slope \(b_c\)), linear polarization resistance (LPR) and corrosion current (\(I_{\text{corr}}\)) values are given in Table 5. When carbon steel is immersed in Sea water the corrosion potential is -962 mV vs saturated calomel electrode (SCE). The corrosion current is 1.561\(\times\)10\(^{-4}\) A/cm\(^2\). When TMA (250 ppm) and Zn\(^{2+}\) (50 ppm) are added to the above system the corrosion potential is shifted to the anodic side from -962 mV to -630 mV. This suggests that the anodic reaction is controlled predominantly. Moreover, in presence of the inhibitor system, the corrosion current decreases from 1.561\(\times\)10\(^{-7}\) A/cm\(^2\) to 7.481\(\times\)10\(^{-6}\) A/cm\(^2\) and
LPR value increases from $1.070 \times 10^5$ ohm cm$^2$ to $1.514 \times 10^6$ ohm cm$^2$. These observations indicate the formation of protective film on the metal surface [17-20].

3.4. Surface Analysis

The structure of Thiomalic acid is shown in fig 3. It contains C=O and O-H stretching vibrations. The protective film formed on the surface of the metal in the presence of Thiomalic acid system and Thiomalic acid–Zn$^{2+}$ system in sea water has been analysed by FT-IR spectroscopy.

3.4.1. Analysis of FT-IR Spectra

FTIR spectrum (KBr) of pure Thiomalic acid (TMA) is shown in Fig 3. The C=O stretching frequency of carboxyl group appears at 1700 cm$^{-1}$. The O-H stretching frequency of TMA appears at 3180 cm$^{-1}$ and the other peak S-H at 2559.46 cm$^{-1}$. The FTIR spectrum (KBr) of film formed on the surface of metal after immersion in sea water containing 250 ppm of TMA and 50 ppm of Zn$^{2+}$ is shown in Fig. 4. The C=O stretching frequency of carboxyl group has shifted from 1700 cm$^{-1}$ to 1594 cm$^{-1}$. The O-H stretching frequency of TMA has shifted from 3180 cm$^{-1}$ to 3425 cm$^{-1}$. The S-H stretching frequency of TMA has shifted from 2559.46 cm$^{-1}$ to 2403.32 cm$^{-1}$. This indicates that these groups have coordinated with Fe$^{2+}$, resulting in the formation of Fe$^{2+}$-TMA complex on the anodic sites of the metal surface. The peak at 1402 cm$^{-1}$ is due to Zn(OH)$_2$ formed on the cathodic sites of the metal surface. Thus FTIR spectra study lead to the conclusion that the Fe$^{2+}$ - TMA complex formed on anodic sites of the metal surface controlled the anodic reaction and Zn(OH)$_2$ formed on the cathodic sites of the metal surface controlling the cathodic reaction[21-24]
Inhibition of corrosion ... thiomalic acid-Zn$^{2+}$ system

SK Selvaraj et al.,

Fig. 3. FT-IR Spectrum of Pure TMA

Fig. 4. FT-IR Spectrum of Sea Water+250ppm of TMA+50ppm of Zn$^{2+}$

3.4.2. Scanning electron microscopy (SEM)

The scanning electron micrographs of carbon steel are shown in Fig 5. The SEM micrograph of polished carbon steel surface (control) is shown in Fig 5a. This shows the smoothness of the metal surface. This implies the absence of any corrosion product formed on the metal surface. The SEM micrograph of carbon steel immersed in seawater is shown in Fig 5b. This shows the roughness of the metal surface by the corrosive environment and the porous layer of corrosion product is present. Pits are observed on the metal surface. Fig 5c shows that the presence of 250 ppm of TMA and 50 ppm of Zn$^{2+}$ in seawater gives the formation of thick films on the carbon steel surface. This may be interpreted as due to the adsorption of the inhibitor on the metal surface incorporating into the passive film in order to block the active site present on the carbon steel surface[25-28].
3.5. Mechanism of corrosion inhibition

The results of weight loss study show that the formulation consists of 250 ppm TMA and 50 ppm \( \text{Zn}^{2+} \) has 96% IE, in controlling corrosion of carbon steel in sea water. A synergistic effect exists between TMA and \( \text{Zn}^{2+} \). Polarization study reveals that TMA – \( \text{Zn}^{2+} \) system functions as anodic inhibitor controlling anodic reaction predominantly and controls anodic reaction to some extent. FTIR spectra reveal that the protective film consists of \( \text{Fe}^{2+} \) - TMA complex and \( \text{Zn(OH)}_2 \). SEM studies confirm the formation of protective film on the metal surface. The effective synergistic formulation consists of 250 ppm of TMA, 50 ppm of \( \text{Zn}^{2+} \) and 50 ppm of CTAB shows IE 98% and 100 % BE. Also the effective synergistic formulation consists of 250 ppm of TMA, 50 ppm of \( \text{Zn}^{2+} \) and 50 ppm of CTAB shows IE 96% and 100 % BE.

The addition of TMA reduces metal dissolution in an aqueous environment and this may be due to adsorption and complex formation at the metal surface with the combined application of TMA and \( \text{Zn}^{2+} \). Hence the corrosion process is inhibited.

The mechanism can be generalized as follows.

When the formulation consists of TMA (250 ppm) and \( \text{Zn}^{2+} \) (50 ppm) is added in Sea water there is a formation of TMA – \( \text{Zn}^{2+} \) complex in solution.

When carbon steel is immersed in this solution, TMA – \( \text{Zn}^{2+} \) complex diffuses from
Inhibition of corrosion ... thiomalic acid - Zn²⁺ system

SK Selvaraj et al.,

the bulk of the solution towards the metal surface.

TMA – Zn²⁺ complex is converted into TMA – Fe²⁺ complex on the anodic sites of the metal surface with the release of Zn²⁺ ion.

\[ \text{TMA} - \text{Zn}^{2+} + \text{Fe}^{2+} \rightarrow \text{TMA} - \text{Fe}^{2+} + \text{Zn}^{2+} \]

The released Zn²⁺ combined with OH⁻ to form Zn(OH)₂ on the cathodic sites of the metal surface.

\[ \text{Zn}^{2+} + 2 \text{OH}^- \rightarrow \text{Zn(OH)}_2 \downarrow \]

Thus the protective film consists of TMA – Fe²⁺ complex and Zn(OH)₂.

In near neutral aqueous solution, the anodic reaction is the formation of Fe²⁺. This anodic reaction is controlled by the formation of TMA – Fe²⁺ on the anodic sites of the metal surface. The cathodic reaction is the generation of OH⁻. It is controlled by the formation of Zn(OH)₂ on the cathodic sites of the metal surface.

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2 \text{e}^- \text{(anodic reaction)} \]
\[ \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 + 2 \text{e}^- \rightarrow 2 \text{OH}^- \text{(cathodic reaction)} \]

\[ \text{Fe}^{2+} + \text{TMA} \rightarrow \text{TMA} - \text{Fe}^{2+} \text{complex} \]
\[ \text{Zn}^{2+} + 2 \text{OH}^- \rightarrow \text{Zn(OH)}_2 \downarrow \]

This accounts for the synergistic effect of TMA – Zn²⁺ system.

4. CONCLUSION

- The Weight–loss study reveals that the formulation consisting of 50ppm of Zn²⁺ and 250ppm of TMA has 96% inhibition efficiency, for one-day system and explains the Synergistic effect between TMA and Zn²⁺ complexes.
- The protective film consists of Fe²⁺ -TMA and Zn(OH)₂ is explained by FT-IR spectroscopy.
- The results of polarization study show that the anodic reaction is controlled predominantly indicating the reduction of dissolution metal as more Thiomalic acid molecules are transported to the cathodic sites in the presence of Zn²⁺ ions, which results in increase in LPR values and decrease in corrosion current [29-35].
- SEM confirm the presence of a protective film on the metal surface.
REFERENCES

Inhibition of corrosion ... thiomalic acid - Zn²⁺ system

SK Selvaraj et al.,


Received: 25-03-2016
Accepted: 29-03-2016
Inhibition of corrosion ... thiomalic acid - Zn²⁺ system

SK Selvaraj et al.,

Prof SK Selvaraj flanked by Prof S Rajendran and Prof M Pandiarajan

Prof Dr A John Amalraj with Prof Erika Kalman (Hungary), during EUROCORR 2003 at Hungary