ROLE OF Zn\textsuperscript{2+} IN ENHANCING THE INHIBITION EFFICIENCY OF TRISODIUM CITRATE

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The inhibition efficiency (IE) of trisodium citrate (TSC)-Zn\textsuperscript{2+} system in controlling corrosion of mild steel in well water has been evaluated by weight loss method. A synergistic effect exists between TSC and Zn\textsuperscript{2+}. The formulation consisting of 50 ppm of TSC and 25 ppm of Zn\textsuperscript{2+} provides 87% of IE. FTIR spectra reveal that the protective film consists of Fe\textsuperscript{2+}-TSC complex and Zn(OH)\textsubscript{2}. Polarization of study confirms the formation of a protective film on the metal surface. The inhibitor system controls the cathodic reaction predominantly.

MATERIALS AND METHODS

Metal specimens

Mild steel specimen was used in the present study. (Composition (wt %): 0.026 S, 0.06 P, 0.4 Mn, 0.1 C and balance iron. The dimension of the specimen was 1 x 4 x 0.2 cm. The molecular structure of trisodium citrate is shown in scheme 1.

Scheme 1. Structure of trisodium citrate

The inhibition efficiency of TSC-Zn\textsuperscript{2+} system in controlling corrosion of mild steel in well water (Table 1) has been evaluated.

Table 1. Parameters of well water

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.38</td>
</tr>
<tr>
<td>Conductivity</td>
<td>3110 ( \mu )( \Omega )\textsuperscript{-1} cm\textsuperscript{-1}</td>
</tr>
<tr>
<td>Chloride</td>
<td>665 ppm</td>
</tr>
<tr>
<td>Sulphate</td>
<td>14 ppm</td>
</tr>
<tr>
<td>TDS</td>
<td>2013 ppm</td>
</tr>
<tr>
<td>Total hardness</td>
<td>1100 ppm</td>
</tr>
</tbody>
</table>

Weight –Loss Method

Mild steel specimens in triplicate were immersed in 100 ml of well water containing various concentration of TSC in the presence and absence of Zn\textsuperscript{2+} for three days. The weight of the specimens before and after immersion was determined using a Shimadzu balance, model AY62. The corrosion products were cleansed with Clarke’s solution \textsuperscript{24}. 

Introduction

Metals are extracted from their ores by reduction process. When metals come in contact with the environment, especially oxygen and moisture, they deteriorate. This process, we call, corrosion. Corrosion is the desire of pure metals to go back to its original state of ores. Corrosion is a natural, spontaneous and thermodynamically stable process. The process of corrosion can be controlled but it cannot be prevented. There are many methods by which corrosion can be controlled one such method is the use of inhibitors. These inhibitors when added in small quantity, decrease the rate of corrosion. Corrosion inhibitors usually contain polar groups with atoms such as nitrogen, sulphur and oxygen. Correspondingly inhibitors include a wide list of organic and inorganic compounds\textsuperscript{1} containing the functional groups such as aldehydes,\textsuperscript{2} amines,\textsuperscript{3,4} amino acids,\textsuperscript{5,6} nitrocompounds,\textsuperscript{7,8} amides,\textsuperscript{9,10} ester,\textsuperscript{11,12} thio compounds,\textsuperscript{13,14} phosphates,\textsuperscript{15,16} phosphonates,\textsuperscript{17,18} ketones,\textsuperscript{19,20} and carboxylic acids\textsuperscript{21-23} Trisodium citrate has carboxyl groups and hydroxyl groups. Such compounds are expected to have good inhibition efficiency.

The present work in undertaken (i) to evaluate the inhibition efficiency of trisodium citrate (TSC)-Zn\textsuperscript{2+} system in controlling corrosion of mild steel in well water, (ii) to analyse the protective film by FTIR spectroscopy and (iii) to study the mechanistic aspects of corrosion inhibition by polarization study.
The inhibition efficiency (IE, %) was then calculated using the equation:

$$ IE = 100 \times \left[ 1 - \frac{W_2}{W_1} \right] $$

where

- $W_1$: corrosion rate in the absence of the inhibitor,
- $W_2$: corrosion rate in the presence of the inhibitor.

**Potentiodynamic polarization**

Polarization studies were carried out in a CHI – Electrochemical workstation with impedance, Model 660A. A three-electrode cell assembly was used. The three-electrode assembly is shown in Scheme 2. The working electrode was mild steel. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode. From the polarization study, corrosion parameters such as corrosion potential ($E_{corr}$), corrosion current ($I_{corr}$) and Tafel slopes (anodic = $b_a$ and cathodic = $b_c$) and Linear polarization resistance ($LPR$) were calculated.

**FTIR Spectra**

FTIR spectra were recorded in a Perkin – Elmer1600 spectrophotometer. The film was carefully removed, mixed thoroughly with KBr made into pellets and FTIR spectra were recorded.

**Result and Discussion**

**Analysis of Results of Weight-loss method**

Corrosion rates of mild steel immersed in well water in the absence and presence of tri sodium citrate (TSC) and Zn$^{2+}$ are given in Table 2. It is observed that TSC alone has some inhibition efficiency. As the concentration of TSC increases inhibition efficiency also increases. 50 ppm of TSC has 13% inhibition efficiency and 250 ppm of TSC has 30%.

**Influence of Zn$^{2+}$ on the inhibition efficiency of TSC**

When Zn$^{2+}$ is added to TSC the corrosion inhibition efficiency TSC to a great extent. This suggests that a synergistic effect exists between Zn$^{2+}$ and the inhibitor namely TSC. Similar synergistic effect existing between Zn$^{2+}$ and inhibitors has been reported by several researchers. The synergistic effect between Zn$^{2+}$ and TSC can be explained as follows. When TSC and Zn$^{2+}$ are mixed, Zn$^{2+}$-TSC complex is formed. It is transported towards the metal surface. On the metal surface, Zn$^{2+}$-TSC complex is broken. The released TSC combines with Fe$^{2+}$ (formed on the metal surface due to corrosion process) resulting in the formation of Fe$^{2+}$-TSC complex. Fe$^{2+}$-TSC is more stable than Zn$^{2+}$-TSC.

The released Zn$^{2+}$ combines with OH$^{-}$ formed by cathodic reaction and Zn(OH)$_2$ is precipitated on the cathodic site of the metal surface. The Zn$^{2+}$-TSC bond is strong enough to carry the complex towards the metals surface and it is weak enough to break in presence of Fe$^{2+}$. This accounts for the breaking of Zn$^{2+}$-TSC complex and formation of Fe$^{2+}$-TSC complex.

**Analysis of polarization curve**

Polarization study has been used to know if a protective film is found on the metal surface. If a protective film is formed on the metal surface, the linear polarization resistance ($LPR$) increases and corrosion current decreases.

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**Table 2. Corrosion rates (CR) of mild steel immersed in well water and the inhibition efficiency obtained by weight loss method.**

<table>
<thead>
<tr>
<th>TSC ppm</th>
<th>0 ppm</th>
<th>25 ppm</th>
<th>50 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR</td>
<td>IE%</td>
<td>CR</td>
<td>IE%</td>
</tr>
<tr>
<td>0</td>
<td>a24.67</td>
<td>22.20</td>
<td>10</td>
</tr>
<tr>
<td>50</td>
<td>2a21.46</td>
<td>3.20</td>
<td>60</td>
</tr>
<tr>
<td>100</td>
<td>3a19.74</td>
<td>4.93</td>
<td>50</td>
</tr>
<tr>
<td>150</td>
<td>4a18.50</td>
<td>9.87</td>
<td>60</td>
</tr>
<tr>
<td>200</td>
<td>5a18.25</td>
<td>11.10</td>
<td>50</td>
</tr>
<tr>
<td>250</td>
<td>6a17.27</td>
<td>12.33</td>
<td>50</td>
</tr>
</tbody>
</table>

Immersion period: 3 Days; CR =Corrosion Rate; IE =Inhibition Efficiency
The potentiodynamic polarization curves of mild steel immersed in various test solutions are shown in Fig 1. The corrosion parameters, namely, corrosion potential ($E_{corr}$), Tafel slopes ($b_a = \text{anodic}$, $b_c = \text{cathodic}$), linear polarization resistance ($LPR$) and corrosion current ($I_{corr}$) are given in Table 3.

When mild steel is immersed in well water the corrosion potential is -630 mV vs SCE. The $LPR$ value is 7799.9 ohm cm$^2$. The corrosion current is $5.537 \times 10^{-6}$ A cm$^{-2}$. When inhibitors (TSC 50 ppm + Zn$^{2+}$ 50 ppm) are introduced into the system, the $LPR$ value increases tremendously from 7799.9 to 23589.8 ohm cm$^2$. Increases in $LPR$ value is an indication of formation protective film formed on the metal surface. This is also supported that by the fact that there is a sharp decrease in the corrosion current value; the corrosion current decreases from $5.537 \times 10^{-6}$ to $1.810 \times 10^{-6}$ A cm$^{-2}$. It is observed that the corrosion potential has shifted to the cathodic side (-630 to -659 mV vs SCE), in presence of inhibitors. This suggests that the cathodic reaction is controlled predominantly in presence of inhibitor system.

When 2.5 ml of Zn is added to TSC solution 87% IE is obtained for 50 ppm of TSC. However as the concentration of TSC increases the inhibition efficiency decreases. This is due to the fact that, as the concentration of TSC, the Zn$^{2+}$-TSC complex becomes more stable and bond is not broken in presence of Fe$^{2+}$. This accounts for the decreases in the IE in presence of higher concentration of TSC. Similar reason can be given for the decrease in IE of 50 ppm Zn$^{2+}$-TSC system. It is observed that 50 ppm Zn$^{2+}$-50 ppm TSC system has 60 %IE. However the IE decreases as the concentration of TSC increases.

Analysis of FTIR spectra

FTIR spectroscopy has been used to analyse the protective film formed on the metal surface. The FTIR spectrum of pure TSC is shown in Fig 2(a). The $\text{C=O}$ stretching frequency of the carboxyl group appears at 1647 cm$^{-1}$. The $\text{-OH}$ stretching frequency appears at 3432 cm$^{-1}$. The FTIR spectrum of the film formed on mild steel surface after immersion in the solution containing 50 ppm of TSC and 25 ppm of Zinc is shown in Fig 2(b). It is observed that the $\text{C=O}$ stretching frequency has shifted from 1647 cm$^{-1}$ to 1608 cm$^{-1}$. The $\text{-OH}$ stretching frequency shifted from 3432 cm$^{-1}$ to 3417 cm$^{-1}$. This indicates that the oxygen atoms of the carboxyl group and $\text{-OH}$ have coordinate with Fe$^{2+}$ resulting in the formation of Fe$^{2+}$-TSC complex formed on the anodic sites of the metal surface. The peaks at 1274.92 cm$^{-1}$ and 612.17 cm$^{-1}$ are due to Zn$^{2+}$O bond. The $\text{-OH}$ stretching frequency appears at 3417 cm$^{-1}$. These observation suggest that Zn(OH)$_2$ is formed on the cathodic sites of the metal surface.

Conclusion

The inhibition efficiency (IE) of trisodium citrate(TSC)-Zn$^{2+}$ system is controlling corrosion of mild steel in well water has been evaluated by weight loss method.

A synergistic effect exists between TSC and Zn$^{2+}$. The formulation consisting of 50 ppm of TSC and 50 ppm of Zn$^{2+}$ provides 87% IE. FTIR spectra reveal that the protective film consists of Fe$^{2+}$-TSC complex and Zn(OH)$_2$. Polarization study confirms the formation of protective film on the metal surface. The inhibitor system controls the cathodic reaction predominantly.
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