INVESTIGATION OF INHIBITIVE ACTION OF UREA- ZN$^{2+}$ SYSTEM IN THE CORROSION CONTROL OF CARBON STEEL IN SEA WATER

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Abstract:

The inhibition efficiency (IE) of Urea in controlling corrosion of carbon steel in sea water in the absence and presence of Zn$^{2+}$ has been evaluated by weight loss method. The formulation consisting of 250 ppm urea and 50 ppm Zn$^{2+}$ has 94% IE. It is found that the inhibition efficiency (IE) of urea increases by the addition of Zn$^{2+}$ ion. A synergistic effect exists between urea and Zn$^{2+}$. Polarization study reveals that Urea – Zn$^{2+}$ system controls the cathodic reaction predominantly and suggests the formation of protective film on the metal surface. The nature of the protective film formed on the metal surface has been analyzed by FTIR spectra and AFM analysis. The protective film is found to consist of Fe$^{2+}$ – Urea complex and Zn(OH)$_2$. Based on the above studies a suitable mechanism has been proposed for the corrosion inhibition.

Keywords: Corrosion inhibition, Urea, carbon steel, synergistic effect, FTIR, AFM, sea water

1. Introduction

Corrosion is the deterioration of metals and alloys by electrochemical reaction with its environment. It is a natural phenomenon which cannot be avoided, but it can be controlled and prevented using the suitable preventive measures like metallic coating, anodic protection, cathodic protection and using inhibitors, etc. Inhibitors are playing very good role in the process of corrosion control. The organic inhibitors containing hetero atoms like oxygen, nitrogen, sulphur and phosphorus, etc shows better corrosion inhibition by forming protective layer over the metal surface. Also the corrosion inhibition efficiency follows the order O < N < S < P $^{1-4}$. Among various organic compounds, urea and its derivatives shows significant corrosion inhibition of metals and alloys in corrosive media. As urea molecule (Fig. 1) contains one oxygen and two nitrogen atoms, hence urea and its derivatives can act as very good corrosion inhibitors $^{5-7}$.

Fig. 1. Structure of urea
The aim of the present study was to investigate synergistic corrosion inhibition for the urea and Zn\(^{2+}\) combination to carbon steel in sea water collected from Bay of Bengal at Marina beach which is located at Chennai, Tamil Nadu, India (Table 1). The corrosion inhibition efficiency was calculated using weight loss method and polarization study. The synergistic effect of the urea – Zn\(^{2+}\) system has been studied using synergism parameters and F – test. The protective film formed on the metal surface characterized using surface morphological studies such as Fourier Transform Infrared Spectra (FTIR) and atomic force microscopy (AFM).

2. Experimental

2.1. Preparation of the specimens

Carbon steel specimens (0.026% S, 0.06% P, 0.4% Mn and 0.1% C and rest iron) of the dimensions 1.0 X 4.0 X 0.2 cm were polished to a mirror finish and degreased with trichloroethylene and used for the weight-loss method and surface examination studies.

2.2. Weight loss method

Carbon steel specimens in triplicate were immersed in 100 mL of the sea water containing various concentrations of the inhibitor in the presence and absence of Zn\(^{2+}\) for three days. The corrosion product cleaned with Clark’s solution. The parameter of the sea water is given in Table 1. The weights of the specimens before and after immersion were determined using a balance, Shimadzu AY62 model. Then the inhibition efficiency was calculated using the equation (1).

Table 1. Physico – Chemical Parameters of Sea Water

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.66</td>
</tr>
<tr>
<td>Conductivity</td>
<td>44200 µmhos/cm</td>
</tr>
<tr>
<td>Chloride</td>
<td>16050 ppm</td>
</tr>
<tr>
<td>Sulphate</td>
<td>2616 ppm</td>
</tr>
<tr>
<td>TDS</td>
<td>30940 ppm</td>
</tr>
<tr>
<td>Total hardness</td>
<td>2800 ppm</td>
</tr>
<tr>
<td>Calcium</td>
<td>120 ppm</td>
</tr>
<tr>
<td>Sodium</td>
<td>6300 ppm</td>
</tr>
<tr>
<td>Magnesium</td>
<td>600 ppm</td>
</tr>
<tr>
<td>Potassium</td>
<td>400 ppm</td>
</tr>
</tbody>
</table>

\[
IE = 100 \left[1 - \left( \frac{W_1}{W_2} \right) \right] \% \quad (1)
\]

Where \(W_1\) and \(W_2\) are corrosion rate in the absence and presence of the inhibitor respectively. The corrosion rate (CR) was calculated using the equation (2).

\[
CR = \frac{87.5 \cdot W}{D \cdot A \cdot T} \text{ mm/y} \quad (2)
\]

Where \(W = \text{weight loss in mg}, D = 7.87 \text{ g/cm}^3, A = \text{surface area of the specimen (10 cm}^2)\) and \(T = 72 \text{ hrs.}\)

2.3. Synergism parameter

Synergism parameters are indications of synergistic effect existing between the inhibitors. \(S_i\) value is found to be greater than one suggesting that the existence of synergistic effect between the inhibitors.

\[
S_i = \frac{1 - \theta_{1+2}}{1 - \theta'_{1+2}}
\]
Where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \theta_2)$

$\theta_1$ = Surface coverage of inhibitor Urea

$\theta_2$ = Surface coverage of inhibitor Zn$^{2+}$

$\theta'_{1+2}$ = Combined inhibition efficiency of inhibitor Urea and Zn$^{2+}$.

2.4. Analysis of Variance (F – test)

F - test was carried out to investigate whether synergistic effect existing between inhibitor systems is statistically significant. If F - value is above 5.32 for 1,8 degrees of freedom, it was proved to be at statistically significant. If it is below the value of 5.32 for 1,8 degrees of freedom, it was statistically insignificant at 0.05 level of significance confirmed.

2.5. Potentiodynamic Polarization Study

Polarization study was carried out in Electrochemical Impedance Analyzer model CHI 660A using a three electrode cell assembly. The working electrode was used as a rectangular specimen of carbon steel with one face of the electrode of constant 1 cm$^2$ area exposed. A saturated calomel electrode (SCE) was used as reference electrode. A rectangular platinum foil was used as the counter electrodes. Polarization curves were recorded after doing iR compensation. The corrosion parameters such as Tafel slopes (anodic slope $b_a$ and cathodic slope $b_c$), corrosion current ($I_{corr}$) and corrosion potential ($E_{corr}$) values were calculated. During the polarization study, the scan rate (V/s) was 0.005; Hold time at $E_f$ (s) was zero and quiet time (s) was 2.

2.5. Surface Examination Study

The carbon steel specimens were immersed in various test solutions for a period of one day. After one day the specimens were taken out and dried. The nature of the film formed on the surface of metal specimens was analyzed by surface analytical technique, FTIR spectra and AFM.

2.5.1. FTIR Spectra

The carbon steel specimens immersed in various test solutions for one day were taken out and dried. The thin film formed on the metal surface was carefully removed and thoroughly mixed with KBr, so as to make it uniform throughout. The FTIR spectra were recorded in a Perkin – Elmer – 1600 spectrophotometer.

2.5.2. Atomic Force Microscopy (AFM)

The carbon steel specimens immersed in various test solutions for one day were taken out, rinsed with double distilled water, dried and subjected to the surface examination. The surface morphology measurements of the carbon steel surface were carried out by atomic force microscopy (AFM) using SPM Veeco diInnova connected with the software version V7.00 and the scan rate of 0.7 Hz.

3. Results and Discussion

3.1. Analysis of results of weight loss study

The calculated inhibition efficiencies (IE) and corrosion rates of urea in controlling corrosion of carbon steel immersed in sea water both in the absence and presence of Zn$^{2+}$ ion are given in Table 2. Urea alone shows some IE. But the combination of 250 ppm urea and 50 ppm Zn$^{2+}$ shows 94% IE. The calculated value indicates the ability of urea to be a good corrosion inhibitor. The IE is found to be enhanced in the presence of Zn$^{2+}$ ion. This suggests a synergistic effect exists between urea and Zn$^{2+}$ ion.
Table 2. Inhibition efficiencies (IE %) and corrosion rates (mmpy) obtained from urea - Zn\textsuperscript{2+} systems, when carbon steel immersed in sea water.

**Inhibitor system:** Urea + Zn\textsuperscript{2+}  

**Immersion period:** 3 days

<table>
<thead>
<tr>
<th>Urea ppm</th>
<th>Zn\textsuperscript{2+} = 0 ppm</th>
<th>Zn\textsuperscript{2+} = 25 ppm</th>
<th>Zn\textsuperscript{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>0.1124</td>
<td>12</td>
</tr>
<tr>
<td>50</td>
<td>8</td>
<td>0.1034</td>
<td>25</td>
</tr>
<tr>
<td>100</td>
<td>14</td>
<td>0.0966</td>
<td>38</td>
</tr>
<tr>
<td>150</td>
<td>30</td>
<td>0.0786</td>
<td>60</td>
</tr>
<tr>
<td>200</td>
<td>48</td>
<td>0.0584</td>
<td>70</td>
</tr>
<tr>
<td>250</td>
<td>56</td>
<td>0.0494</td>
<td>74</td>
</tr>
</tbody>
</table>

3.2. **Synergism Parameters (S\textsubscript{i})**

The values of synergism parameters are shown in Table 3. Here the values of S\textsubscript{i} are greater than one, suggesting a synergistic effect. S\textsubscript{i} approaches 1 when no interaction exists between the inhibitor compounds. When S\textsubscript{i} > 1, this points to synergistic effects. In the case of S\textsubscript{i} < 1, the negative interaction of inhibitors prevails (i.e. corrosion rate increases). From Table 3, it can be seen that the values of S\textsubscript{i} are greater than unity, suggesting that the phenomenon of synergism existing between urea and Zn\textsuperscript{2+}. Also the synergism parameter (S\textsubscript{i}) for the formulation consisting of 250 ppm of urea and 50 ppm of Zn\textsuperscript{2+} is 6.08, which is greater than one. Thus, the enhancement of the inhibition efficiency caused by the addition of Zn\textsuperscript{2+} to urea is only due to the synergistic effect.
Table 3. Synergism parameters (SI) for carbon steel immersed in sea water in the absence and presence of inhibitor.

**Inhibitor system:** Urea + Zn\(^{2+}\)  
**Immersion period:** 3 days

<table>
<thead>
<tr>
<th>Urea ppm</th>
<th>(\theta_1)</th>
<th>(\theta_{1,2} (Zn^{2+} = 25 \text{ ppm}))</th>
<th>(\theta^{*}_{1,2})</th>
<th>(S_I)</th>
<th>(\theta_1)</th>
<th>(\theta_{1,2} (Zn^{2+} = 50 \text{ ppm}))</th>
<th>(\theta^{*}_{1,2})</th>
<th>(S_I)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.08</td>
<td>0.12</td>
<td>0.19</td>
<td>0.25</td>
<td>1.07</td>
<td>0.08</td>
<td>0.17</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(\theta_1)</td>
<td>(S_I)</td>
<td>(\theta_{1,2})</td>
<td>(\theta^{*}_{1,2})</td>
<td>(S_I)</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0.14</td>
<td>0.12</td>
<td>0.24</td>
<td>0.38</td>
<td>1.22</td>
<td>0.14</td>
<td>0.17</td>
<td>0.28</td>
</tr>
<tr>
<td>150</td>
<td>0.30</td>
<td>0.12</td>
<td>0.38</td>
<td>0.60</td>
<td>1.54</td>
<td>0.30</td>
<td>0.17</td>
<td>0.41</td>
</tr>
<tr>
<td>200</td>
<td>0.48</td>
<td>0.12</td>
<td>0.54</td>
<td>0.70</td>
<td>1.52</td>
<td>0.48</td>
<td>0.17</td>
<td>0.56</td>
</tr>
<tr>
<td>250</td>
<td>0.56</td>
<td>0.12</td>
<td>0.61</td>
<td>0.74</td>
<td>1.48</td>
<td>0.56</td>
<td>0.17</td>
<td>0.63</td>
</tr>
</tbody>
</table>

3.3. **Analysis of Variance (ANOVA)**

To investigate whether, the influence of Zn\(^{2+}\) on the inhibition efficiencies of urea is statistically significant, F – test was carried out. The results are given in Table 4. The results of Analysis of Variance (ANOVA) shows the influence of 25 ppm and 50 ppm of Zn\(^{2+}\) on the inhibition efficiencies of 50 ppm, 100 ppm, 150 ppm, 200 ppm and 250 ppm of urea. The obtained F – value 2.75 for 25 ppm Zn\(^{2+}\), is not statistically significant, since it is less than the critical F – value 5.32 for 1, 8 degrees of freedom at 0.05 level of significance. Therefore, it is concluded that the influence of 25 ppm of Zn\(^{2+}\) on the inhibition efficiencies of various concentrations of urea is not statistically significant. The obtained F – value 8.11 for 50 ppm Zn\(^{2+}\), is statistically significant, since it is greater than the critical F – value 5.32 for 1, 8 degrees of freedom at 0.05 level of significance. Therefore, it is concluded that the influence of 50 ppm Zn\(^{2+}\) on the inhibition efficiencies of various concentrations of urea is statistically significant.

Table 4. Distribution of F – value between the inhibition efficiencies of various concentrations of Urea – Zn\(^{2+}\) system.

<table>
<thead>
<tr>
<th>Zn(^{2+}) (ppm)</th>
<th>Sources of Variance</th>
<th>Sum of Squares</th>
<th>Degrees of Freedom</th>
<th>Mean Square</th>
<th>F</th>
<th>Level of Significance of F</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>Between</td>
<td>242</td>
<td>1</td>
<td>242</td>
<td>2.75</td>
<td>p&lt;0.05</td>
</tr>
<tr>
<td></td>
<td>Within</td>
<td>704</td>
<td>8</td>
<td>88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>Between</td>
<td>722</td>
<td>1</td>
<td>722</td>
<td>8.11</td>
<td>p&gt;0.05</td>
</tr>
<tr>
<td></td>
<td>Within</td>
<td>711</td>
<td>8</td>
<td>89</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.4. Analysis of Polarization curves

The potentiodynamic polarization curves of carbon steel immersed in sea water in the absence and presence of inhibitors are shown in Fig 2. The calculated corrosion parameters such as corrosion potential ($E_{corr}$), Tafel slopes (anodic slope $b_a$ and cathodic slope $b_c$), linear polarization resistance and corrosion current ($I_{corr}$) values are given in Table 5. When carbon steel is immersed in sea water the corrosion potential is $-731$ mV vs saturated calomel electrode (SCE). The corrosion current is $3.80 \times 10^{-4}$ A/cm$^2$. When urea (250 ppm) and Zn$^{2+}$ (50 ppm) are added to the above system the corrosion potential is shifted to the cathodic side (from $-731$ mV to $-783$ mV). This suggests that the cathodic reaction is controlled predominantly. Moreover in presence of the inhibitor system, the corrosion current decreases from $3.80 \times 10^{-4}$ A/cm$^2$ to $3.23 \times 10^{-4}$ A/cm$^2$ and LPR value increases from $1.0756 \times 10^4$ ohm cm$^2$ to $1.4451 \times 10^4$ ohm cm$^2$. These observations indicate the formation of protective film on the metal surface $^{17-20}$.

Table 5. Corrosion Parameters of carbon steel immersed in sea water in the absence and presence of inhibitors obtained by polarization method

<table>
<thead>
<tr>
<th>Urea Ppm</th>
<th>Zn$^{2+}$ ppm</th>
<th>$E_{corr}$ mV vs SCE</th>
<th>$b_a$ mV/decade</th>
<th>$b_c$ mV/decade</th>
<th>LPR ohm cm$^2$</th>
<th>$I_{corr}$ A/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>-731</td>
<td>135.5</td>
<td>162.3</td>
<td>$1.0756 \times 10^4$</td>
<td>$3.80 \times 10^{-4}$</td>
</tr>
<tr>
<td>250</td>
<td>50</td>
<td>-783</td>
<td>146.0</td>
<td>200.7</td>
<td>$1.4451 \times 10^4$</td>
<td>$3.23 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Fig. 2. Polarization curves of carbon steel immersed in various test solutions
(a) Sea water (b) Sea water + Urea (250 ppm) + Zn$^{2+}$ (50 ppm)

3.5. Analysis of FTIR spectra

The FTIR spectrum of pure urea is shown in Fig. 3 (a). The C=O stretching frequency is appears at 1677 cm$^{-1}$. The N – H stretching and deformation frequencies appear at 3455 cm$^{-1}$ and 1625 cm$^{-1}$ respectively. The C – N stretching frequency appears at 1453 cm$^{-1}$. The FTIR spectrum of the film formed on the metal surface after immersion in marine media consisting urea (250 ppm) and Zn$^{2+}$ (50 ppm) is shown in Fig. 3 (b). The C=O stretching frequency has shifted from 1677 cm$^{-1}$ to 1660 cm$^{-1}$. The N – H stretching frequency has shifted from 3455 cm$^{-1}$ to 3434 cm$^{-1}$. The N – H deformation frequency has shifted from 1625 cm$^{-1}$ to 1639 cm$^{-1}$. The C – N
stretches frequency has shifted from 1453 cm$^{-1}$ to 1413 cm$^{-1}$. This indicates that the urea has coordinated with Fe$^{2+}$ on the metal surface through oxygen atom of C=O group and nitrogen atom of N – H group resulting in the formation of Fe$^{2+}$ - Urea complex. The peak at 1386 cm$^{-1}$ is due to Zn – O stretching. These observations indicate the presence of Zn(OH)$_2$ formed on the metal surface. Thus the FTIR study leads to the conclusion that the protective film consist of Fe$^{2+}$ - Urea complex and Zn(OH)$_2$ formed on the metal surface 21-24.

![Fig. 3. (a) FTIR Spectrum of pure Urea](image)

![Fig. 3. (b) FTIR Spectrum of the film formed on the metal surface](image)

### 3.6. Atomic force microscopy (AFM)

Atomic force microscopy is a powerful technique for the gathering of roughness statistics from a variety of surfaces 25-26. AFM is becoming an accepted method of roughness investigation 27-31. All atomic force microscopy (AFM) images were obtained using SPM Vecco dlinova AFM instrument operating in contact mode in air. The scan size of all the AFM images is 4.91 µm x 4.91 µm areas at a scan rate of 0.7 Hz. The two dimensional (2D), three dimensional (3D) AFM morphologies and the AFM cross-sectional profile for polished carbon steel surface (reference sample), carbon steel surface immersed in sea water (blank) and carbon steel surface immersed in sea water containing the formulation of 250 ppm of Urea and 50 ppm of Zn$^{2+}$ are shown as Fig.4. (a, d, g), (b, e, h), (c, f, i) respectively.
3.6.1. Root-mean-square roughness, average roughness and peak-to-valley value

AFM images analysis was performed to obtain the average roughness, $R_a$ (the average deviation of all points roughness profile from a mean line over the evaluation length), root-mean-square roughness, $R_q$ (the average of the measured height deviations taken within the evaluation length and measured from the mean line) and the maximum peak-to-valley (P-V) height values (largest single peak-to-valley height in five adjoining sampling heights) \(^{32}\). $R_q$ is much more sensitive than $R_a$ to large and small height deviations from the mean \(^{33}\). The summary of the average roughness ($R_a$), rms roughness ($R_{rms}$) and maximum peak-to-valley height (P-V) value for carbon steel surface immersed in various test solutions are given in Table 6.

The value of $R_a$, $R_q$ and P-V for the polished carbon steel surface (reference sample) are 5.6241 nm, 8.1069 nm and 44.40 nm respectively, which shows a more homogeneous surface, with some places in where the height is lower than the average depth \(^{34}\). Fig. 4. (a, d, g) displays the uncorroded metal surface. The slight roughness observed on the polished carbon steel surface is due to atmospheric corrosion. The average roughness, rms roughness and P-V height values for the carbon steel surface immersed in sea water are 32.9000 nm, 40.2000 nm and 140.60 nm respectively. These data suggests that carbon steel surface immersed in sea water has a greater surface roughness than the polished metal surface, which shows that unprotected carbon steel surface is rougher and was due to the corrosion of the carbon steel in sea water. Fig. 4. (b, e, h) displays corroded metal surface with few pits.

Table 6. AFM data for carbon steel surface immersed in inhibited and uninhibited environments

<table>
<thead>
<tr>
<th>Samples</th>
<th>Average ($R_a$) Roughness (nm)</th>
<th>RMS ($R_q$) Roughness (nm)</th>
<th>Maximum peak-to-valley (P-V) height (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polished carbon steel (control)</td>
<td>5.6241</td>
<td>8.1069</td>
<td>44.40</td>
</tr>
<tr>
<td>Carbon steel immersed in sea water</td>
<td>32.9000</td>
<td>40.2000</td>
<td>140.60</td>
</tr>
<tr>
<td>Carbon steel immersed in sea water containing Urea (250 ppm) and Zn(^{2+}) (50 ppm)</td>
<td>10.4000</td>
<td>14.5000</td>
<td>72.38</td>
</tr>
</tbody>
</table>

The presence of 250 ppm of Urea and 50 ppm of Zn\(^{2+}\) in sea water reduced the $R_{rms}$ by a factor of 2.77 (14.5000 nm) from 40.2000 nm and the average roughness is significantly reduced to 7.1882 nm when compared with 32.9000 nm of carbon steel surface immersed in sea water. The maximum peak-to-valley height also was reduced to 72.38 nm. These parameters confirm that the surface appears smoother. The smoothness of the surface is due to the formation of a compact protective film of Fe\(^{2+}\) - Urea complex and Zn(OH)\(_2\) on the metal surface thereby inhibiting the corrosion of carbon steel. Also the above parameter observed are somewhat greater than the AFM data of polished metal surface which confirms the formation of the film on the metal surface, which is protective in nature.
Fig. 4. 2D AFM images of carbon steel surface.
(a) Polished carbon steel (control)
(b) Carbon steel immersed in sea water (blank)
(c) Carbon steel immersed in sea water containing Urea (250 ppm) + Zn\(^{2+}\) (50 ppm)
Fig. 4. 3D AFM images of carbon steel surface.
(a) Polished carbon steel (control)
(b) Carbon steel immersed in sea water (blank)
(c) Carbon steel immersed in sea water containing Urea (250 ppm) + Zn$^{2+}$ (50 ppm)
4. Mechanism of corrosion inhibiton

With these discussions, a mechanism is proposed for the corrosion inhibition of carbon steel immersed in sea water 250 ppm of Urea and 50 ppm of Zn$^{2+}$.

- When the formulation consisting of 250 ppm of urea and 50 ppm of Zn$^{2+}$ in sea water there is a formation of urea – Zn$^{2+}$ complex in solution.
- When carbon steel is immersed in this solution urea – Zn$^{2+}$ complex diffuses from the bulk of the solution towards the metal surface.
- Urea – Zn$^{2+}$ complex is converted into urea – Fe$^{2+}$ complex on the anodic sites of the metal surface with the release of Zn$^{2+}$ ion.
  \[
  \text{Zn}^{2+} \text{– Urea + Fe}^{2+} \rightarrow \text{Fe}^{2+} \text{– Urea + Zn}^{2+}
  \]
- The released Zn$^{2+}$ combines with OH$^-$ to form Zn(OH)$_2$ on the cathodic sites of the metal surface.
  \[
  \text{Zn}^{2+} + 2 \text{OH}^- \rightarrow \text{Zn(OH)}_2
  \]
- Thus the protective film consists of Fe$^{2+}$ – Urea complex and Zn(OH)$_2$.
- In near neutral aqueous solution the anodic reaction is the formation of Fe$^{2+}$. This anodic reaction is controlled by the formation of Urea – Fe$^{2+}$ complex on the anodic site of the metal surface. The cathodic reaction is the generation of OH$^-$. It is controlled by formation of Zn(OH)$_2$ on the cathodic sites of the metal surface.
  \[
  \begin{align*}
  \text{Fe} & \rightarrow \text{Fe}^{2+} + 2 \text{e}^- \ (\text{Anodic reaction}) \\
  \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 + 2\text{e}^- & \rightarrow 2 \text{OH}^- \ (\text{Cathodic reaction}) \\
  \text{Fe}^{2+} + \text{Urea} & \rightarrow \text{Fe}^{2+} \text{– Urea complex} \\
  \text{Zn}^{2+} + 2 \text{OH}^- & \rightarrow \text{Zn(OH)}_2
  \end{align*}
  \]
This accounts for the synergistic effect of Urea – Zn\(^{2+}\) system.

5. Conclusions

The present study leads to the following conclusions:

The formulation consisting of 250 ppm Urea and 50 ppm Zn\(^{2+}\) shows 94% IE. The synergism parameter and F – test confirms the existence of synergistic effect between urea and Zn\(^{2+}\) ion. The polarization study reveals that Urea – Zn\(^{2+}\) system controls cathodic reaction predominantly. FTIR spectra reveal that the protective film consists of Fe\(^{2+}\) – Urea complex and Zn(OH)\(_2\). The AFM images confirm the formation of protective layer on the metal surface and hence the corrosion process is inhibited.

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References