Corrosion Inhibition by an Ion Pair Reagent-Zn\(^{2+}\) System

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Abstract: Inhibition of corrosion of carbon steel in dam water (Tamil Nadu, India) by Pentane sulphonic acid as its sodium salt (SPS)-Zinc ion system has been studied using weight-loss and potentiodynamic polarization methods. Results of weight loss method indicated that inhibition efficiency (IE) increased with increasing inhibitor concentration. Polarization study reveals that SPS-Zn\(^{2+}\) system functions as a cathodic inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. The nature of protective film formed on the metal surface has been analysed by FTIR spectra and AFM analysis. From the results of above studies a suitable mechanism for corrosion inhibition is proposed.

Keywords: AFM, Carbon steel, Corrosion, Electrochemical techniques, FTIR.

INTRODUCTION

Corrosion plays a very important role in diverse fields of industry and, consequently, in economics. The protection of metals and alloys is thus of particular interest. The goal of studying the processes of corrosion is to find methods of minimizing or preventing it. One approach is the use of corrosion inhibitors. Organic compounds have become widely accepted as effective corrosion inhibitors in various media. Most of the organic inhibitors containing nitrogen, oxygen, sulfur atoms, and multiple bonds in their molecules facilitate adsorption on the metal surface [1-3].

Organic compounds are recognized as effective inhibitors of the corrosion of many metals and alloys. The efficiency of an organic compound as a corrosion inhibitor is closely associated with the chemical adsorption [4-8]. Most of these organic compounds contain nitrogen, sulphur, oxygen and multiple bonds in the molecules which are adsorbed on the metal surface and the organic compound [9,10]. Much interest has been devoted to organic inhibitors such as polyethylene glycols [11], 1,2,3 benzotriazoles [12], 2 mercaptobenzimidazole [13], ethoxylated fatty acids [14] and meta substituted aniline-N- salicylidenes [15]. It was also found that the presence of hetero atom with unsaturated bonds in an organic compound caused inhibitive effect and reduces the metal dissolution. Protecting efficiency was also found to be improved with increasing the length of alkyl chain and the organic compound concentration [16].

A survey of the available literature reveals that the Corrosion inhibition of 2-naphthalesulfonic acid, 2, 7-naphthaledisulfonic acid and 2-naphthol-3, 6-disulfonic acid on iron electrode in sulfuric acid has been investigated [17]. The inhibition action of 2-mercaptobenzoxazol, 2-mercapto benzimidazole, N-cetyl pyridinium bromide and propargyl benzene_sulphonate on the corrosion of carbon steel in acid media have also been studied [18]. Manickavasagam et al., have reported the corrosion inhibition of Poly (Styrene sulphonic acid) - doped poly aniline on carbon steel in acid media [19]. Aliev has described the influence of salts of alkyl phenol Sulphonic acid on the corrosion of ST3 steel [20]. Shakkthivel and Vasudevan have studied the effect of Acrylic acid-diphenylamine sulphonic acid copolymer threshold inhibitor for sulphate and carbonate scales in cooling water systems [21].

Ion pair reagents are used as counter ions in ion pairs in reverse phase liquid chromatography and in reverse phase thin layer chromatography. They have been used in separation and quantitative determination of amino acids and peptides, of nucleosides, of vitamin B\(_4\) compounds, of forensic drugs and of neuropeptides and various other pharmaceutical products. N-alkyl sulphonates interact specifically with biologicals, especially proteins, by virtue of electrostatic interaction along the polar chain or because of their stereochemistry in solution [22].

The medium which is used in the present study is dam water collected from Sothuparai dam in the state of Tamil Nadu, India, constructed across the Vaigai River, the water from which is used by the industries located downstream in cooling systems.

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The present work is undertaken to evaluate the inhibition efficiency (IE) of an ion pair reagent, Sodium pentane sulphonate (SPS) - Zn²⁺ system, in controlling corrosion of carbon steel immersed in dam water in the absence and presence of Zn²⁺ by weight loss method,

1) to study the mechanism of corrosion inhibition by Polarization study and AC impedance spectra,
2) to analyse the protective film by FTIR spectra and Atomic Force Microscope and
3) to propose the mechanism of corrosion inhibition based on the above results.

MATERIALS AND METHODOLOGY

Preparation of the Specimen

Carbon steel specimens of size 1.0 cm × 4.0 cm × 0.2 cm and chemical composition 0.026 % Sulphur, 0.06 % Phosphorous, 0.4 % Manganese, 0.1 % Carbon and the rest iron, (specimen density 7.87 gm/cm³), were polished to a mirror finish and degreased with trichloroethylene and used for the weight loss method and surface examination studies.

Weight-Loss Method

Carbon steel specimens were immersed in 100 ml of the water containing various concentrations of the inhibitor (Sodium 1-Pentane Sulphonate) in the absence and presence of Zn²⁺ for 3 days. The molecular structure of Sodium 1-pentane sulphonate is given below.

The weights of the specimens before and after immersion were determined using a Digital Balance (Model AUY 220 SHIMADZU). The corrosion products were cleaned with Clarke’s solution prepared by dissolving 20 gms of Sb₂O₃ and 50 gms of SnCl₂ in one litre of concentrated Hydrochloric acid of specific gravity (1.9) [23].

The corrosion IE was calculated using the equation,

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

where \( W_1 \) is the weight loss value in the absence of inhibitor and \( W_2 \) is the weight loss value in the presence of inhibitor.

Corrosion rate was calculated using the formula,

\[ \text{Mils penetration per year (mpy)} = \frac{534 W}{DAT} \]  
(2)

where Mils penetration per year is the rate of penetration in milli inches per year which is the customary unit for corrosion rate

\( W = \) weight loss in milligrams
\( D = \) density of specimen in g/cm³
\( A = \) area of specimen in square inches
\( T = \) exposure time in hours

Surface Examination Study

The carbon steel specimens were immersed in various test solutions for a period of 1 day. After 1 day, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimen was analyzed by various surface analysis techniques.

Fourier Transform Infrared Spectra

These spectra were recorded in a Perkin-Elmer-1600 spectrophotometer using KBr pellet. The FTIR spectrum of the protective film was recorded by carefully removing the film, mixing it with KBr and making the pellet.

Atomic Force Microscopy Characterization (AFM)

The carbon steel specimen immersed in blank and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water, dried and subjected to surface examination. Atomic force microscopy (Veeco dinnova model) was used to observe the surface of the samples in tapping mode, using cantilever with linear tips. The scanning area in the images was 5 μm × 5 μm and the scan rate was 0.6 Hz/second

Potentiodynamic Polarization

Polarization studies were carried out in a CHI-electrochemical work station with impedance model 660A. It was provided with iR compensation facility. A three electrodes cell assembly was used. The working electrode was carbon steel. A SCE was the reference electrode. Platinum was the counter electrode. From polarisation study, corrosion parameters such as corrosion potential (Ecorr), corrosion current (Icorr), Tafel slopes anodic = ba and cathodic = bc were calculated and linear polarization study (LPR) was done. The scan rate (V/s) was 0.01. Hold time at Ef (s) was zero and quiet time (s) was two.

AC Impedance Spectra

The instrument used for polarization study was used to record AC impedance spectra also. The cell set up was also the same. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies. Values of charge transfer resistance (Rt) and the double layer capacitance (Cdl) were calculated. AC impedance spectra were recorded with initial E(v) = 0, high frequency (Hz) = 1x10⁵, low frequency (Hz) = 1, amplitude (V) = 0.005 and quiet time (s) = 2.

RESULTS AND DISCUSSION

Weight-Loss Study

The physicochemical parameters of dam water (Tamil Nadu, India) are given in Table 1.

The corrosion inhibition efficiencies and the corresponding corrosion rates (mpy) of Sodium pentane sulphonate (SPS)-Zn²⁺ systems are given in Table 2.

The inhibition efficiencies of SPS-Zn²⁺ systems are given in Table 2. It is found that the IE increases as the concentration of SPS increases. As the concentration of Zn²⁺ increases, IE also increases. A synergistic effect exists between SPS and Zn²⁺. For example, 250 ppm of SPS has 22%IE. 30 ppm of Zn²⁺ has 21% IE. However, interestingly, the formulation consisting of 250 ppm of SPS and 30 ppm of Zn²⁺ has 68% IE. That is mixture of inhibitors shows better inhibition efficiency than the individual inhibitors [24].

![Image](image1.png)
Corrosion Inhibition by an Ion Pair Reagent-Zn\textsuperscript{2+} System

Table 1. Water Analysis (Sothuparai Dam Water, Tamil Nadu, India)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Brownish</td>
</tr>
<tr>
<td>Total dissolved solids</td>
<td>100 ppm</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>140 μmhos/cm</td>
</tr>
<tr>
<td>pH</td>
<td>8.25</td>
</tr>
<tr>
<td>Total hardness as CaCO\textsubscript{3}</td>
<td>50 ppm</td>
</tr>
<tr>
<td>Calcium</td>
<td>10 ppm</td>
</tr>
<tr>
<td>Magnesium</td>
<td>06 ppm</td>
</tr>
<tr>
<td>Iron</td>
<td>1.2 ppm</td>
</tr>
<tr>
<td>Nitrate</td>
<td>10 ppm</td>
</tr>
<tr>
<td>Chloride</td>
<td>10 ppm</td>
</tr>
<tr>
<td>Sulphate</td>
<td>02 ppm</td>
</tr>
</tbody>
</table>

Table 2. Inhibition Efficiencies (IE) and the Corrosion Rates (CR) of Carbon Steel Immersed in Dam Water in the Presence of SPS-Zn\textsuperscript{2+} System

<table>
<thead>
<tr>
<th>Inhibitor SPS (ppm)</th>
<th>Zn\textsuperscript{2+} (ppm)</th>
<th>IE %</th>
<th>CR mpy</th>
<th>IE %</th>
<th>CR mpy</th>
<th>IE %</th>
<th>CR mpy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>15</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-</td>
<td>4.4384</td>
<td>12</td>
<td>3.9058</td>
<td>21</td>
<td>3.5063</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>07</td>
<td>4.1277</td>
<td>16</td>
<td>3.7283</td>
<td>47</td>
<td>2.3524</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>11</td>
<td>3.9502</td>
<td>20</td>
<td>3.5507</td>
<td>49</td>
<td>2.2636</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>13</td>
<td>3.8614</td>
<td>17</td>
<td>3.6389</td>
<td>54</td>
<td>2.0416</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>19</td>
<td>3.5951</td>
<td>24</td>
<td>2.3732</td>
<td>61</td>
<td>1.7320</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>22</td>
<td>3.4620</td>
<td>26</td>
<td>3.2844</td>
<td>68</td>
<td>1.4203</td>
<td></td>
</tr>
</tbody>
</table>

Analysis of Polarization Curves

The potentiodynamic polarization curves of carbon steel immersed in various test solutions are shown in Fig. (1). The corrosion parameters are given in Table 3. When carbon steel is immersed in dam water, the corrosion potential is −494 mV vs SCE. The formulation consisting of 250 ppm SPS + 30 ppm Zn\textsuperscript{2+} shifts the corrosion potential to −573 mV vs SCE. This suggests that the cathodic reaction is controlled predominantly. The corrosion current value and LPR value for dam water are 2.66×10\textsuperscript{-6} A/cm\textsuperscript{2} and 2.05×10\textsuperscript{4} Ω cm\textsuperscript{2}.

For the formulation of SPS (250 ppm) + Zn\textsuperscript{2+} (30 ppm), the corrosion current value has decreased to 4.96×10\textsuperscript{-7} A/cm\textsuperscript{2}, and the LPR value has increased to 7.70×10\textsuperscript{4} Ω cm\textsuperscript{2}. This indicates that a protective film is formed on the metal surface. When a protective film is formed on the metal surface LPR value increases and corrosion current value decreases [25-29].

Analysis of AC Impedance Spectra

AC impedance spectra have been used to detect the formation of film on the metal surface. If a protective film is formed, the charge transfer resistance (R\textsubscript{ct}) increases and double layer capacitance (C\textsubscript{dl}) value decreases [30-34]. The AC impedance spectra of carbon steel immersed in various solutions are shown in Fig. (2). The AC impedance parameters, namely charge transfer resistance (R\textsubscript{ct}) and double layer capacitance (C\textsubscript{dl}) are given in Table 4. When carbon steel is immersed in dam water, R\textsubscript{ct} value is 1.084×10\textsuperscript{4} Ω cm\textsuperscript{2} and C\textsubscript{dl} value is 8.24×10\textsuperscript{-10} F/cm\textsuperscript{2}. When SPS and Zn\textsuperscript{2+} are added to dam water, R\textsubscript{ct} value increases from 1.084×10\textsuperscript{4} Ω cm\textsuperscript{2} to 1.396×10\textsuperscript{4} Ω cm\textsuperscript{2} and the C\textsubscript{dl} decreases from 8.24×10\textsuperscript{-10} F/cm\textsuperscript{2} to 6.38×10\textsuperscript{-10} F/cm\textsuperscript{2}. This suggests that a protective film is formed on the surface of the metal. This is further supported by the increase in impedance value from 4.062 to 4.128 log(z/ohm) (Fig. 3). This accounts for the very high IE of SPS-Zn\textsuperscript{2+} system.

Analysis of FTIR Spectra

Researchers have confirmed that FTIR spectrometer is a powerful instrument that can be used to determine the type of bonding for organic inhibitors adsorbed on the metal surface [33-37]. FTIR spectra have been used to analyze the
protective film formed on metal surface. FTIR spectrum of pure SPS is shown in Fig (4a). The FTIR spectrum of the film formed on the metal surface after immersion in the dam water for one day containing 250 ppm of SPS and 30 ppm of Zn$^{2+}$ is shown in Fig (4b). The S=O stretching frequency of SPS has decreased from 1194 cm$^{-1}$ to 1123 cm$^{-1}$. This indicates that the oxygen atom of S=O group has coordinated with Fe$^{2+}$ formed on the metal surface resulting in the formation of Fe$^{2+}$-SPS complex on the anodic sites of the metal surface. The peak at 1397 cm$^{-1}$ is due to Zn-O stretching. The stretching frequency due to –OH appears at 3419 cm$^{-1}$. So, it is concluded that Zn (OH)$_2$ is formed on cathodic sites of the metal surface [38-40].

Table 4. Impedance Parameters of Carbon Steel in Dam Water in the Presence and Absence of Inhibitor Obtained by AC Impedance Method

<table>
<thead>
<tr>
<th>SPS (ppm)</th>
<th>Zn$^{2+}$ (ppm)</th>
<th>$R_t$ (Ω cm$^2$)</th>
<th>$C_{dl}$ (F/cm$^2$)</th>
<th>Impedance log(z/ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1.084*10$^4$</td>
<td>8.24*10$^{-10}$</td>
<td>4.062</td>
</tr>
<tr>
<td>250</td>
<td>30</td>
<td>1.3960*10$^4$</td>
<td>6.38*10$^{-10}$</td>
<td>4.128</td>
</tr>
</tbody>
</table>

Fig. (2). AC impedance spectra of carbon steel immersed in various test solutions. a) Dam water. b) Dam water containing 250 ppm of SPS and 30 ppm of Zn$^{2+}$.

Atomic Force Microscopy Characterization

AFM is a powerful technique to investigate the surface morphology at nano-to micro-scale and has become a new choice to study the influence of inhibitor on the generation and the progress of the corrosion at the metal/solution interface [41-43]. 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 dam water (blank sample) and carbon steel surface immersed in dam water containing the formulation of 250 ppm of SPS and 30 ppm of Zn$^{2+}$ are shown as Fig. (5) images (a, d, g), (b, e, h), (c, f, i) respectively.

Fig. (3). AC impedance spectra of carbon steel immersed in various test solutions. (Frequency Bode plots). a) Dam water. b) Dam water containing 250 ppm of SPS and 30 ppm of Zn$^{2+}$.

Root-Mean-Square Roughness, Average Roughness and Peak-to-Valley Value

AFM image analysis was performed to obtain the average roughness, $R_q$ (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) [41]. Table 5 is a summary of ($R_q$), ($R_q$), (P-V) value for carbon steel surface immersed in different environment.

Fig. (4). FTIR spectra a) pure sodium pentane sulphonate, b) film formed on metal surface after immersion in dam water containing 250 ppm of SPS and 30 ppm of Zn$^{2+}$.

Fig. (5a, d, g) displays the surface topography of uncorroded metal surface. The values of $R_q$, $R_q$ and P-V height for the polished carbon steel surface (reference sample) are 4.3 nm, 3.4 nm and 35.3 nm respectively.
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Slight roughness observed on the polished carbon steel surface is due to atmospheric corrosion.

Fig. (5b, e, h) displays the corroded metal surface with few pits in the absence of the inhibitor immersed in dam water. The (R\textsubscript{q}), (R\textsubscript{a}), (P-V) height values for the carbon steel surface are 31.9nm, 24.9nm and 420.3 nm respectively. These data suggests that carbon steel surface immersed in dam water has a greater surface roughness than the polished metal surface, which shows that the unprotected carbon steel surface is rougher and was due to the corrosion of the carbon steel in dam water environment.

Fig. (5c, f, i) displays the steel surface after immersion in dam water containing 250 ppm of SPS and 30 ppm of Zn\textsuperscript{2+}. The (R\textsubscript{q}), (R\textsubscript{a}), (P-V) height values for the carbon steel...
Zn\(^{2+}\) – SPS \(\rightarrow\) Fe\(^{2+}\) ----------> Fe\(^{2+}\) – SPS \(\rightarrow\) Zn\(^{2+}\)

When the formulation consisting of 250 ppm of SPS and 30 ppm of Zn\(^{2+}\) in dam water is prepared there is formation of SPS– Zn\(^{2+}\) complex in solution.

1) When carbon steel is immersed in this solution SPS– Zn\(^{2+}\) complex diffuses from the bulk of the solution towards the metal surface.

2) SPS– Zn\(^{2+}\) complex is converted into SPS– Fe\(^{2+}\) complex on the anodic sites of the metal surface with the release of Zn\(^{2+}\) ion.

\[ \text{Zn}^{2+} – \text{SPS} + \text{Fe}^{2+} \rightarrow \text{Fe}^{2+} – \text{SPS} + \text{Zn}^{2+} \]

3) The released Zn\(^{2+}\) combines with OH\(^-\) to form Zn(OH)\(_2\) on the cathodic sites of the metal surface Zn\(^{2+}\) + 2 OH\(^-\) \(\rightarrow\) Zn(OH)\(_2\) ↓

4) Thus the protective film consists of SPS– Fe\(^{2+}\) complex and Zn(OH)\(_2\).

5) This account for the synergistic effect of SPS – Zn\(^{2+}\) system.

Similar mechanism has been proposed by Noreen Antony et al., [36] while studying Inhibition and biocide actions of Sodium dodecyl sulfate- Zn\(^{2+}\) system for the corrosion of carbon steel in chloride solution and by Sathiyabama et al., [44] while studying Methyl orange as corrosion inhibitor for carbon steel in well water.

**Mechanism of Corrosion Inhibition**

With these discussions, a mechanism may be proposed for the corrosion inhibition of carbon steel immersed in dam water by 250 ppm SPS and 30 ppm Zn\(^{2+}\) system.

When the formulation consisting of 250 ppm of SPS and 30 ppm of Zn\(^{2+}\) in dam water is prepared there is formation of SPS– Zn\(^{2+}\) complex in solution.

**CONCLUSIONS**

The present study leads to the following conclusions

The inhibition efficiency (IE) of SPS in controlling corrosion of carbon steel immersed in dam water in the absence and presence of Zn\(^{2+}\) has been evaluated by weight loss method. The formulation consisting of 250 ppm SPS and 30 ppm Zn\(^{2+}\) has 68% IE. Polarization study reveals that SPS – Zn\(^{2+}\) system functions as a cathodic inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectra reveal that the protective film consists of Fe\(^{2+}\) – SPS complex and Zn(OH)\(_2\).

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**CONFLICT OF INTEREST**

None declared.

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