

# Influence of Carbon Steel Microstructure on the Performance of Sodium Potassium Tartrate-Zn<sup>2+</sup> as Corrosion Inhibitors in RO Water

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## ABSTRACT

The Inhibition Efficiency (IE) of Sodium - Potassium Tartrate (SPT), in controlling corrosion of carbon steel in RO water in the absence and presence of Zn<sup>2+</sup> has been evaluated by mass-loss method. The formulation consisting of 175ppm SPT and 10ppm Zn<sup>2+</sup> has 92.1% IE. It is found that the Inhibition efficiency of SPT increases with the addition of Zn<sup>2+</sup> ion. A synergistic effect exists between SPT and Zn<sup>2+</sup>. Polarization and surface characterization analyses study and FT-IR spectrum confirm the protection of the carbon steel surface by inhibitive film. A suitable mechanism for corrosion inhibition has been proposed based on the results obtained from the above studies.

**Keywords :** Carbon Steel, Sodium- Potassium Tartrate, RO Water, Corrosion inhibition.

## I. INTRODUCTION

Carbon and low-alloy steels are the major construction materials extensively used in water distribution, petroleum, power production, as well as chemical and electrochemical industries [1], [2] and [3]. However, iron-based alloys are subject to corrosion, especially pitting corrosion in neutral or acidic solutions containing aggressive anions [4]. Corrosion events result in economic loss and even serious operational problem [5].

Metals used in industrial applications are protected from corrosion in different ways, apart from surface treatment such as coating [6]. Corrosion of carbon steel is a subject of fundamental, academic and industrial concern and has been received a considerable attention during the last few decades [7]. Corrosion, scale and fouling problems can appear when water containing chlorides is used as thermal fluid. This problem can occur jointly, reducing the thermal efficiency of the cooling circuit with the significant socio-economic repercussions. Many inhibitors have been used in cooling water systems in order to solve these problems [8-10]. Gomma and Gamal [11] studied the effect of (0.05 M) tartaric and malic acids on the corrosion behavior of (0.5% C) carbon steel in the absence and in the presence of Fe<sup>2+</sup> at pH 2.8 by measuring the corrosion potential and the

corrosion rates using galvanostatic polarization technique. The extent to which corrosion is promoted depends on the concentration of Fe<sup>2+</sup> ion. Tartaric acid has a more pronounced effect on the corrosion rate. Gluconates and gluconic acid are known to be effective, non-toxic inhibitors for iron and mild steel in cooling water systems [12-17].

The RO product water in pipelines, when comes into contacts with pumps, valves or other metallic components, has the capability to corrode these Components. A survey of the literature indicates that although numerous references are available on corrosion resistant materials but only limited references are available on carbon steel related to RO product water [18-20].

A mixture of sodium gluconate and borate have shown an inhibition effect on the dissolution of mild steel in the near neutral media [21]. Though SPT and Zn<sup>2+</sup> ion crystal used as corrosion protection in many cases like cooling water systems, no study can be explained about the binary system present in RO water.

The objective of this work was designed to study the synergistic behaviour of sodium potassium tartrate (SPT) and Zn<sup>2+</sup> as corrosion inhibitors on carbon steel in RO

water using three different techniques: mass-loss, electrochemical studies, surface analysis techniques, hoping to get some general ideas to guide the composing of inhibitor in reality.

## II. METHODS AND MATERIAL

### 2. Experimental Details

#### 2.1. Preparation of the Specimen

Carbon steel specimens (0.026% S, 0.6% P, and 0.4 % Mn, 0.1% C, and rest iron) of the dimensions 1.0 cm X 4.0 cm X 0.2 cm were polished to a mirror finish and degreased with trichloroethylene and used for the mass-loss method and surface examination studies.

A stock solution of 1000 ppm of SPT was prepared in bidistilled water and the desired concentration was obtained by appropriate dilution. The concentration of SPT used for the study ranges from 10 to 200ppm. All solutions were prepared using RO water (Karur, Tamil Nadu, India). The study was carried out at room temperature. The physico-chemical parameters of RO water is given in Table 1.

**Table1.** Physico- chemical parameters of RO water used to prepare solutions

S.No	Parameters	Level of content
1	Appearance	Colorless and clear
2	Odour	None
3	TDS	200 ppm
4	pH	7.5
5	Total hardness as CaCO <sub>3</sub>	200 ppm
6	Chloride as Cl	200 ppm
7	Fluoride as F	Nil
8	Sulphate as SO <sub>4</sub>	Nil
9	Phosphate as PO <sub>4</sub>	Nil

#### 2.2. Mass-loss method

Carbon steel specimens were immersed in 100ml of the RO water, containing various concentration of the inhibitor in the absence and presence for 7 days. The

weight 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.

The Corrosion IE was then calculated using the equation.  
% of IE = 100 [1-(W<sub>2</sub> / W<sub>1</sub>)]

Where W<sub>1</sub> is the corrosion rate in the absence of inhibitor and W<sub>2</sub> is the corrosion rate in the presence of inhibitor. Corrosion rate was calculated using the above formula.

$$\text{Corrosion rate} = 87.6 W / \text{DAT mmy}^{-1} \text{ [22]}$$

W = Mass- loss, milligrams

D = density of specimen, g / cm<sup>3</sup>

A= area of specimen, cm<sup>2</sup>

T = exposure, hours = 168 hrs

#### 2.3. Potentiodynamic polarization technique

Polarization studies were carried out in a CHI – electrochemical workstation with impedance model 660 A. It was provided with IR facility. A three electrode cell assemble was used and the working electrode was carbon steel. A SCE was the reference electrode. Platinum was the counter electrode. From polarization study, corrosion parameters such as corrosion potential (E<sub>corr</sub>), corrosion current (I<sub>corr</sub>) (Tafel slopes anodic = β<sub>a</sub> and cathodic = β<sub>c</sub>) were calculated and a linear polarization study was done. The scan rate (V /S) was 0.01. Hold time at E<sub>fcs</sub> was zero and quit time (s) was two.

#### 2.4. AC Impedance technique

Electrochemical impedance spectra in the form of Nyquist plots were recorded at OCP in the frequency range from 60KHz to 10MHz with 4 to 10 steps per decade. A sine wave, with 10mV amplitude, was used to perturb the system. The impedance parameters viz., charge transfer resistance (R<sub>ct</sub>), double layer capacitance (C<sub>dl</sub>) were obtained from the Nyquist plots.

#### 2.5. Surface examination techniques

The carbon steel specimens were immersed in blank as well as inhibitor solutions, for a period of 7 days. After

the immersion period is over, the specimens were taken out and dried. The nature of the thin film formed on the surface of the metal specimen analyzed by various surface analysis techniques. The morphology of carbon steel specimen surface (corroded and inhibited) was studied by recording SEM images of the corresponding samples using OXFORD Instruments analytical scanning electron microscope.

### III. RESULTS AND DISCUSSION

#### 3.1. Mass-loss method

Mass-loss measurements of the carbon steel in RO water in the absence and presence of different concentrations of the inhibitors were carried out and the results are reported in Table 2. When the concentration of SPT increased from 10ppm to 200ppm, I.E increases from 30 to 92.1 % at 10ppm Zn<sup>2+</sup>. The formulation 10ppm Zn<sup>2+</sup> + 175ppm SPT shows the maximum I.E. Beyond the Concentration of 175ppm SPT, I.E decreases due to the desorption of inhibitor molecules into bulk of the solution from the metal surface. When 10 ppm Zn<sup>2+</sup> was used alone, Inhibition efficiency is 5.5% only and 175ppm SPT alone, Inhibition efficiency is 23.0 % only. When the two above was combined, the Inhibition efficiency is 92.1 %. From below results, it is clear that there exists a synergism.

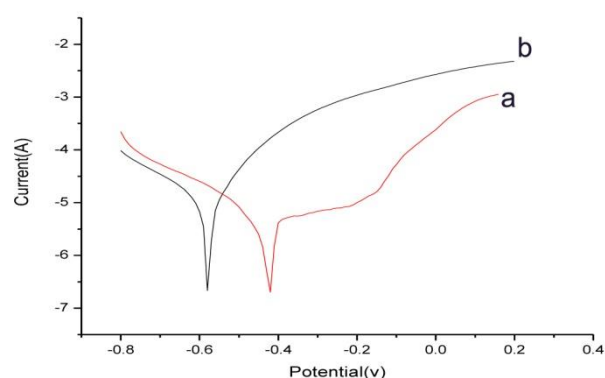
**Table. 2** Corrosion Rates of Carbon steel in RO water in the absence and presence of SPT and Zn<sup>2+</sup> ions

Concentration (ppm)		Corrosion Rate (mmy <sup>-1</sup> )	Inhibition efficiency (%)
Zn <sup>2+</sup>	SPT		
Blank	-	171.5	-
<b>10</b>	<b>-</b>	<b>162</b>	<b>5.5</b>
-	-	135	21.0
<b>-</b>	<b>175</b>	<b>132.6</b>	<b>23.0</b>
10	10	120.5	30.0
10	50	115.6	32.5
10	75	85.5	50.0
10	100	50	71.0
10	125	34	80.0
10	150	26.5	84.5
<b>10</b>	<b>175</b>	<b>13.5</b>	<b>92.1</b>
10	200	21	88.0

#### 3.2. Analyses of Polarization Curves

Polarization study has been used to confirm the type of inhibition during corrosion inhibition processes [23-26]. The potentiodynamic polarization curves of carbon steel immersed in RO water in the absence and presence of inhibitors are shown in Fig1. The corrosion parameters are given in Table 3.

It was found that the values of corrosion current density (I<sub>corr</sub>) of carbon steel in the presence of inhibitor were smaller than without addition of inhibitor (Fig. 1). Furthermore, as presented in Fig.1b, the addition of 10ppm Zn<sup>2+</sup> + 175ppm SPT shifts the corrosion potential (E<sub>corr</sub>) value (from -593.466mV to -417.659mV) in studied inhibitor system. According to Ferreira and W.H. Li, if the displacement in corrosion potential is more than 85mV with respect to the corrosion potential of the blank, the inhibitor can be seen as cathodic or anodic type [27-28]. The corrosion potential shift in more anodic mode and maximum displacement was <85mV which indicated that the studied inhibitor system can be classified as anodic inhibitor.



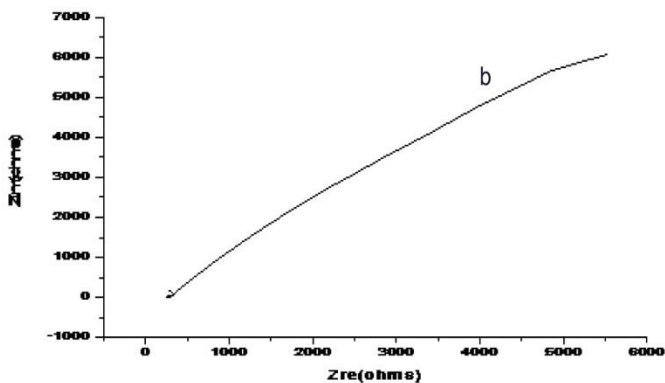
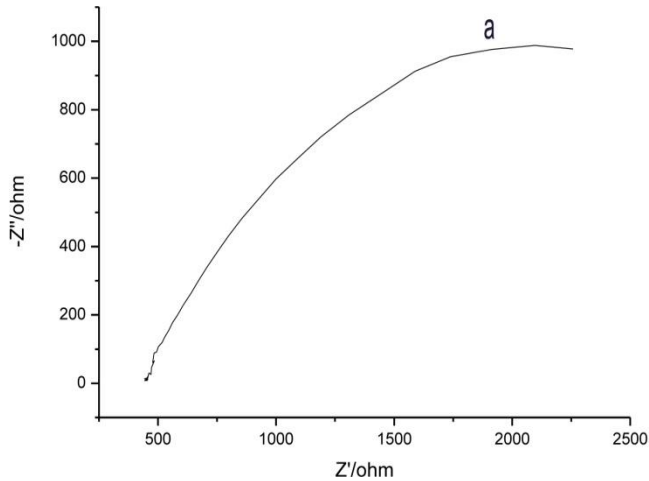
**Figure 1.** Tafel plots of carbon steel immersed in RO water a) Blank b) Presence of binary inhibitor system (10ppm Zn<sup>2+</sup> + 175ppm SPT)

**Table 3.** Tafel corrosion parameters for carbon steel in RO water in the absence and presence of the binary inhibitor formulations

Concentration on ppm		E <sub>corr</sub> mV vs SCE	β <sub>a</sub> mV/de c	β <sub>c</sub> mV/de c	I <sub>corr</sub> μA/c m <sup>2</sup>	IE %
Zn <sup>2+</sup>	SPT					

Blank	-	593.466	649.068	91.98	190.397	-
10	175	417.659	209.387	161.653	9.564	94

### 3.3. Analyses of Electrochemical Impedance Spectroscopy



**Figure 2.** Nyquist plots of carbon steel immersed in RO water a) Blank b) Presence of binary inhibitor system (10ppm Zn<sup>2+</sup> + 175ppm SPT)

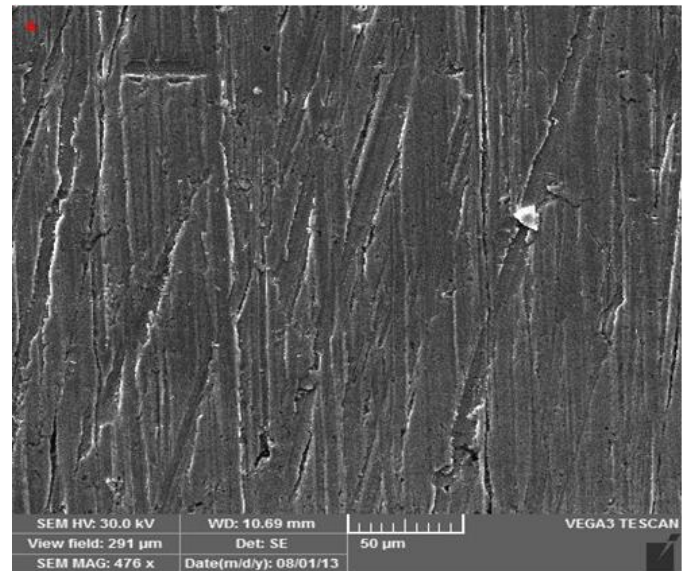
Figure 2 (a-b) shows in it is clear that the impedance curves are significantly changed with the presence of inhibitor. It is also found that from the Nyquist plot, even with the addition (or) absence of inhibitor does not alter the style of impedance curves, thus proposing a similar mechanism of inhibition is involved. It can be seen from the figure, that the obtained Nyquist curves is due to the charge transfer process, mostly control the corrosion of carbon steel. The low frequency inductive

loop is owing to the growth and dissolution of the surface layer [29-30]. The impedance parameters derived from these plots are given in Table 4. As noted from Table 4, the charge transfer resistance values ( $R_{ct}$ ) substantially increased, and double layer capacitance ( $C_{dl}$ ) decreased when 10ppm Zn<sup>2+</sup> and 175ppm SPT added as inhibitors.

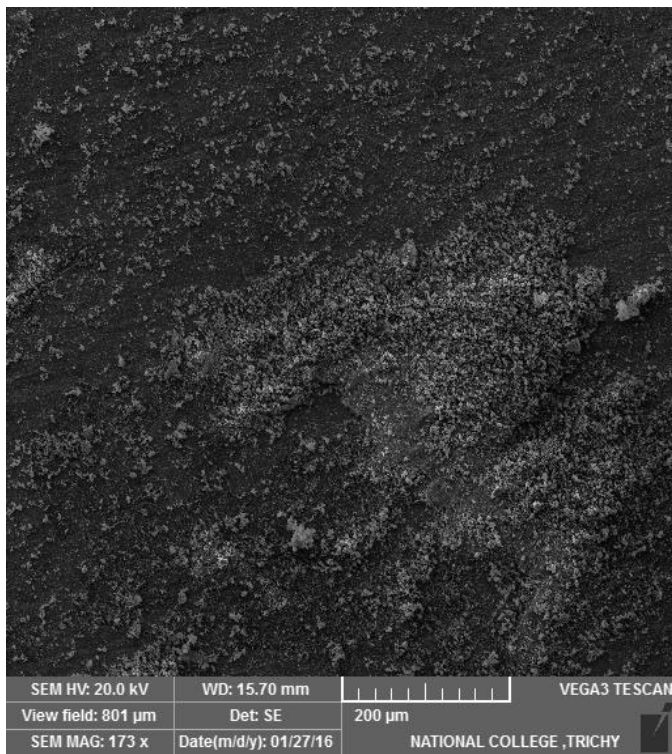
**Table 4.** Impedance parameters for carbon steel in RO water in the absence and presence of the binary inhibitor formulation (10ppm Zn<sup>2+</sup> + 175ppm SPT)

Concentration (ppm)		Charge transfer resistance $R_{ct}$ ( $\Omega$ )	Double layer Capacitance ( $C_{dl}$ ) $\mu\text{F}/\text{cm}^2$	I.E %
Zn <sup>2+</sup>	SPT			
Blank	-	950	$7.3 \times 10^{-5}$	-
10	175	10750	$8.9 \times 10^7$	91.16

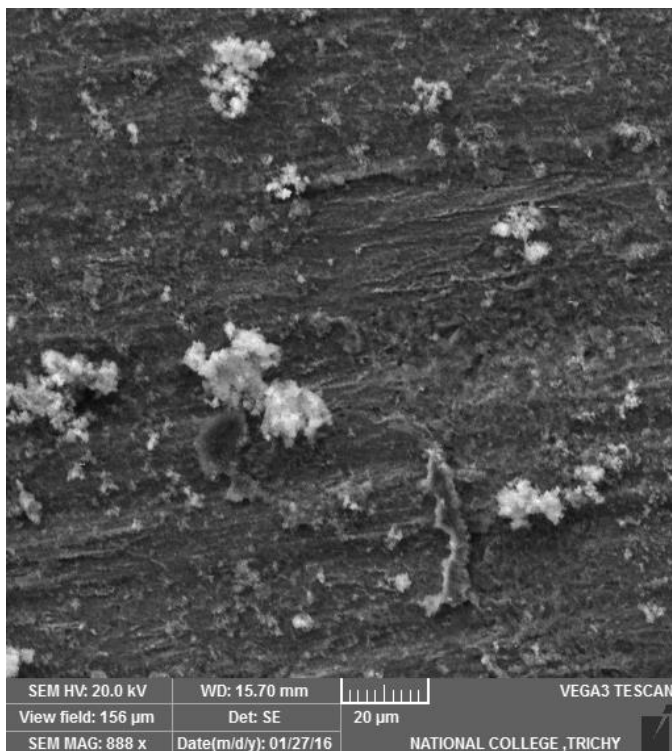
### 3.4 Analyses of SEM



(a)



(b)

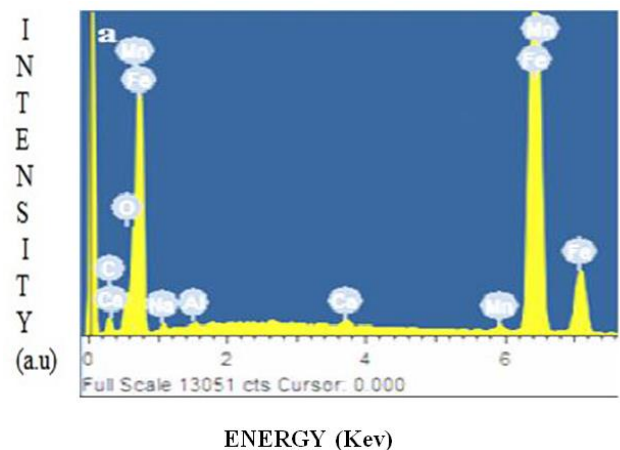


(c)

The scanning electron microscope images further supported the formation of a protective film by the inhibitors and their interaction with surface atoms of carbon steel [31]. The images of carbon steel surface immersed in RO water in the absence and presence of inhibitors are shown in Fig.3 Figure 3a illustrates the morphology of the polished carbon steel surface before exposure to corrosion environment. The micrograph shows a characteristic inclusion, which is probably an oxide inclusion. Figure 3b shows SEM image of the surface of the studied carbon steel electrode specimen after immersion in RO water. The micrograph reveals that the surface is strongly damaged. The corroded areas are shown as grey and white zones, which correspond to the dandruff of iron oxide. It suggests an uncovered surface of metal electrode severely corroded. The highly oxidized phase has perhaps been formed in air when desiccated under no protection of the surface.

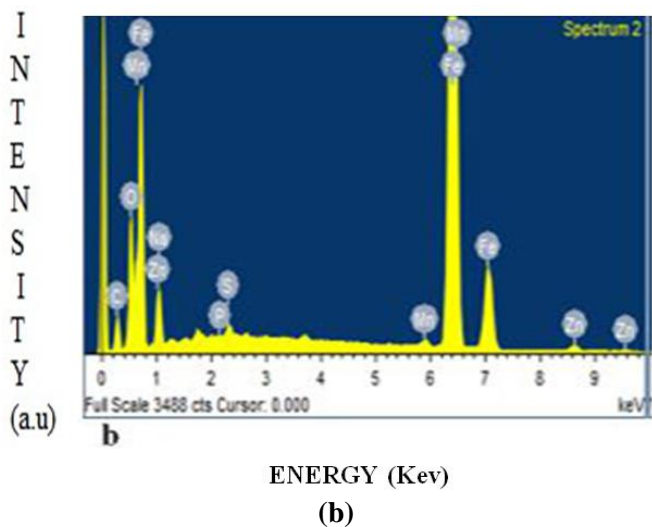
Figure 3c shows SEM image for the surface of another carbon steel specimen after immersion for the same time interval in RO water which contain binary formulation. The micrograph reveals that the inhibited metal surface is smoother than the uninhibited surface because of the presence of a good protective film on the metal surface. This confirms the highest inhibition efficiency of the inhibitor.

### 3.5. Analyses of Energy Dispersive X-ray (EDX)



(a)

**Figure 3.** SEM images of a) Polished carbon steel b) blank c) Presence of binary inhibitor formulation (10ppm Zn<sup>2+</sup> + 175ppm SPT)

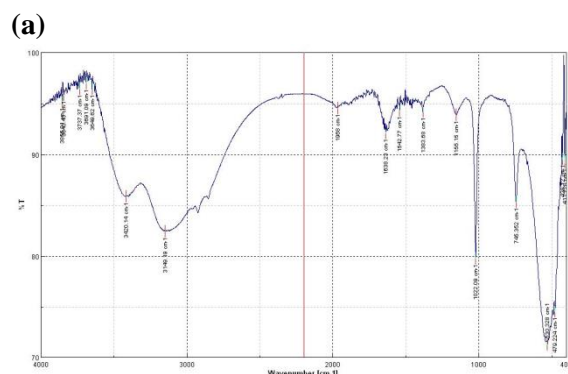
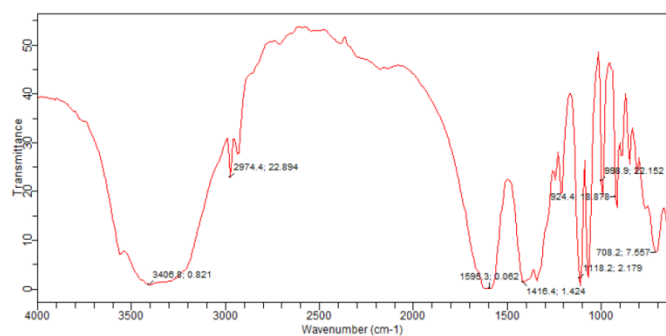


**Figure 4.** EDX spectra of carbon steel a) in the absence of inhibitor formulation b) in the presence of binary system (10ppm Zn<sup>2+</sup> + 175ppm SPT)

### 3.5. Analyses of Energy dispersive X-Ray (EDX)

The protective film formed on carbon steel surface was analysed using EDX is shown in Figure 4a shows highly weakened peaks and corrosion products present on to the metal surface.

### 4. Analyses of FT-IR spectra



(b)

FT-IR spectra have been used to analyze the protective film formed on metal surface [32-34]. The FT-IR spectrum of pure SPT (a) is shown that the C=O stretching frequency of the carboxyl group appears at 1595.3 cm<sup>-1</sup>. The OH stretching frequency appears at 3406.8 cm<sup>-1</sup>. The C-H stretching frequency appears at 2974.4 cm<sup>-1</sup>. The FT-IR spectrum of film (KBr) formed on the surface of carbon steel after immersion in the test solution containing 10ppm of Zn<sup>2+</sup> and 175 ppm of SPT (b) is shown that C=O stretching frequency shifted from 1595.3cm<sup>-1</sup> to 1638.23 cm<sup>-1</sup>, O-H stretching frequency shifted from 3406.8 cm<sup>-1</sup> to 3420.14 cm<sup>-1</sup> and C-H stretching frequency shifted from 2974.4 cm<sup>-1</sup> to 3149.19 cm<sup>-1</sup>. This indicates that oxygen atom of carboxyl group and OH have coordinated with Fe<sup>2+</sup> resulting in the formation of Fe<sup>2+</sup> - SPT complex formed on the anodic sites of the metal surface at 1383.68 cm<sup>-1</sup>[35].

### 5. Mechanism of Corrosion Inhibition

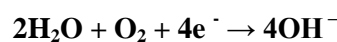
An analysis of the results of mass - loss method reveals the inhibitor formulation consisting of 10ppm of Zn<sup>2+</sup> and 175ppm of SPT offers an I.E of 92.1%. Results of polarization study suggest that the formulation functions as an anodic inhibitor.

From the above observations, the following mechanism of corrosion inhibition is proposed. When carbon steel specimen is immersed in RO water,

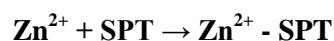
The anodic reaction is



and the cathodic reaction is

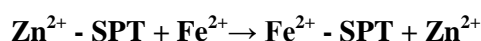


When the inhibitor system consisting of 10ppm of Zn<sup>2+</sup> and 175ppm of SPT is prepared, there is a formation of Zn<sup>2+</sup> -SPT complex in solution.

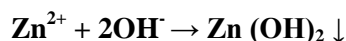


When the carbon steel is immersed in the solution, the Zn<sup>2+</sup> - SPT complex diffuses from the bulk of the solution to the metal surface. On the surface of the metal,

$Zn^{2+}$  - SPT complex is converted into  $Fe^{2+}$  - SPT complex at the local anodic regions.



The released  $Zn^{2+}$  ions combine with  $OH^-$  ions to form  $Zn(OH)_2$  on the anodic sites.



Thus the protective film consists of  $Fe^{2+}$  - SPT complex,  $Zn(OH)_2$  and oxides of Fe.

#### IV. CONCLUSION

The present study leads to the following conclusions

1. The  $Zn^{2+}$ -SPT system shows a synergistic effect in controlling the corrosion of carbon steel immersed in RO water.
2. The binary formulation has good inhibition efficiency for the corrosion of carbon steel in RO water.
3. Polarization study reveals that the formulation  $Zn^{2+}$ -SPT functions as an anodic inhibitor.
4. SEM, EDX, AC Impedance and FT-IR study corroborated that the inhibitor molecules are adsorbed onto the metal surface.

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