

Research Article

Electrochemical and AFM Study of Corrosion inhibition of Carbon Steel by Octanesulphonic acid-Zinc Ion System

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Abstract

The corrosion inhibition efficiency of octane sulphonic acid as its sodium salt $C_8H_{17}SO_3Na$ (SOS) in combination with a bivalent cation like Zinc ion (Zn^{2+}) in controlling corrosion of carbon steel immersed in dam water have been evaluated by weight loss method. A significant decrease in the corrosion rate was observed in presence of the investigated inhibitor system. The formulation consisting of 1.16×10^{-3} mol/l of (SOS) and 1.04×10^{-4} mol/l of Zn^{2+} offers the maximum inhibition efficiency (IE=88 %) to carbon steel. A synergistic effect exists between SOS and Zn^{2+} . As the immersion period increases IE decreases. AC impedance spectra reveal that a protective film is formed on the metal surface. These observations have been supported by surface morphology studies using atomic force microscopy (AFM) carried out on the carbon steel samples in the absence and presence of inhibitor.

Keywords: Carbon steel, Corrosion inhibition, Synergistic effect, surface morphology, atomic force microscopy

1. Introduction

Carbon steel has been widely employed as a construction material for pipe work in the oil and gas production, such as down hole tubulars, flow lines and transmission pipelines (Jiang *et al.*, 2006 ; Villamizar *et al.*, 2007; Papavinasam *et al.*, 2007) However, one of the major problems related to its use is its low corrosion resistance in these environment. (Alsabagh *et al.*, 2006).

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 which facilitate adsorption on the metal surface (Badr, 2009; Al-Sarawy *et al.*, 2008; Gao *et al.*, 2007).

The mechanism of how organic corrosion inhibitors work is not known. In most cases, empirical testing has provided information on the effectiveness of a particular molecule as a corrosion inhibitor for a certain substrate in a certain medium. Knowledge of the surface chemistry of

adsorbed organics is important for elucidating the mechanism of inhibitor action and to achieve this, surface analytical techniques are required. 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 improve with increasing the length of alkyl chain and the organic compound concentration (Srhiri *et al.*, 1996).

A survey of the available literature reveals that the corrosion inhibition of 2-naphthalenesulfonic acid, 2, 7-naphthalenedisulfonic acid and 2-naphthol-3, 6-disulfonic acid on iron electrode in sulfuric acid was investigated. (Vracar *et al.*, 2002). The inhibition action of 2-mercaptobenzoxazol, 2- mercapto benzimidazole, N- cetyl pyridinium bromide and propargyl benzene sulphonate on the corrosion of mild steel in acid media have also been studied (Prakash Rajesh *et al.*, 2006). The corrosion inhibition of Poly (styrene sulphonic acid) - doped poly aniline on mild steel in acid media have been reported (Manickavasagam *et al.*, 2002). The influence of salts of Alkyl phenol Sulphonic acid on the corrosion of ST3 steel has been described (Aliev, 2008). The effect of Acrylic acid-diphenylamine sulphonic acid copolymer threshold inhibitor for sulphate and carbonate scales in cooling water systems have been studied (Shakkthivel and Vasudevan, 2006).

The aim of the present study is to evaluate, understand and discuss the mechanism of corrosion protection by sodium octane sulphonate (SOS) - Zn^{2+} system on carbon

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steel in aqueous medium using weight loss method and AC impedance spectroscopy. The morphology of the protective film was examined by atomic force microscopy (AFM).

The medium which is used in the present study is dam water collected from the 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.

2. Experimental

The chemicals used in this study, sodium octane sulphonate (inhibitor) and $ZnSO_4 \cdot 7H_2O$ (Zn^{2+} ions) co inhibitor were AR grade.

2.1. Preparation of the specimen

Carbon steel specimens of size $1.0 \text{ cm} \times 4.0 \text{ cm} \times 0.2 \text{ cm}$, (area 10 cm^2) and chemical composition 0.026 % Sulphur, 0.06 % Phosphorous, 0.4 % Manganese, 0.1 % Carbon and the rest iron (density 7.87 gm/cm^3), 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 were immersed in 100 ml of the medium containing various concentrations of the inhibitor (Sodium 1-Octane Sulphonate) in the absence and presence of Zn^{2+} for 3 days. 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 Sb_2O_3 and 50 gms of $SnCl_2$ in one litre of Conc.HCl of specific gravity (1.9) (Wranglen, 1985). The corrosion IE was then calculated using the equation

$$IE = 100 [1 - (W_2/W_1)] \%$$

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 (Fontana, 2006)

$$\text{millimeter per year (mm/year)} = 87.6W / DAT \quad (1)$$

where, W = weight loss in milligrams, D = density of specimen g/cm^3 , A = area of specimen in square cm and T = exposure time in hours.

2.3. AC impedance spectra

The AC impedance studies were carried out in a CHI-electrochemical work station with impedance model 660A. It was provided with iR compensation facility. A three electrode cell assembly was used. The working electrode was carbon steel. Saturated calomel electrode was the reference electrode. Platinum was the counter electrode. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies. Values of charge transfer resistance (R_t) and the double

layer capacitance (C_{dl}) were calculated.

$$R_t = (R_s + R_t) - R_s \quad (2)$$

where R_s = solution resistance

$$C_{dl} = 1/2\pi R_t f_{max} \quad (3)$$

where f_{max} = frequency at maximum imaginary impedance.

AC impedance spectra were recorded with initial $E_{(v)} = 0$, high frequency (Hz) = 1×10^5 , low frequency (Hz) = 1, amplitude (V) = 0.005 and quiet time (s) = 2.

2.4. Atomic Force Microscopy characterization (AFM)

The carbon steel specimens were immersed in blank and in the inhibitor solution for a period of one day. The specimens were removed, rinsed with double distilled water, dried and subjected to the surface examination. Atomic force microscopy (Veeco diInnova model) was used to observe the samples' surface in tapping mode, using cantilever with linear tips. The scanning area in the images was $5 \mu\text{m} \times 5 \mu\text{m}$ and the scan rate was 0.6 Hz /second

3. Results and Discussion

3.1. Weight-loss study

The physicochemical parameters of dam water are given in Table 1. The corrosion inhibition efficiencies and the corresponding corrosion rates (millimeter per year) of SOS- Zn^{2+} systems are given in Table 2

Table 1 Water Analysis

Parameters	Result
Appearance	Brownish
Total dissolved solids	100 mol/l
Electrical conductivity	140 Micromho/cm
pH	8.25
Total hardness as $CaCO_3$	50 mol/l
Calcium	10 mol/l
Magnesium	06 mol/l
Iron	1.2 mol/l
Nitrate	10 mol/l
Chloride	10 mol/l
Sulphate	02 mol/l

3.1.1. Inhibition efficiency (IE) and the corrosion rates millimeter per year (mm/year) of carbon steel immersed in dam water offered by SOS- Zn^{2+} system; Immersion period -3days

It is found that the IE increases as the concentration of SOS increases. As the concentration of Zn^{2+} increases, IE also increases. A synergistic effect exists between SOS and Zn^{2+} . For example, SOS has an IE of and 33% at a concentration of $1.16 \times 10^{-3} \text{ mol/l}$ and Zn^{2+} has an IE of 21% at a concentration of $1.04 \times 10^{-4} \text{ mol/l}$. However, the formulation consisting of $1.16 \times 10^{-3} \text{ mol/l}$ of SOS and $1.04 \times 10^{-4} \text{ mol/l}$ of Zn^{2+} has 88% IE. i.e. the mixture of inhibitors shows better inhibition efficiency than the individual inhibitors. The improvement in the protection efficiency can be attributed to the formation of a complex

between Zn²⁺ and SOS which results from the synergistic effect between the two inhibitors, Zn²⁺ and SOS. As a result of this complex formation, the inhibitor molecules are readily transported from the bulk to the metal surface (Umamathi et al., 2008).

Table 2 The corrosion inhibition efficiencies and the corresponding corrosion rates (mm/year) of SOS-Zn²⁺ system

Inhibitor SOS (mol/l)	0		5.2×10 ⁻⁵		1.04×10 ⁻⁴	
	IE %	CR mm/year	IE %	CR mm/year	IE %	CR mm/year
0	-	0.1127	12	0.0992	21	0.0891
0.23×10 ⁻³	13	0.0981	31	0.0778	60	0.0451
0.46×10 ⁻³	15	0.0958	38	0.0699	64	0.0383
0.69×10 ⁻³	18	0.0924	36	0.0722	71	0.0327
0.92×10 ⁻³	26	0.0834	38	0.0699	74	0.0293
1.16×10 ⁻³	33	0.0755	43	0.0643	88	0.0135

3.1.2. Synergism Parameter (S_I)

Synergism parameters are indications of synergistic effect existing between inhibitors (Mary Anbarasi et al., 2012; Anuradha et al., 2008).

$$S_I = 1 - I_{1+2} / 1 - I_{1+2}$$

Where

$$I_{1+2} = (I_1 + I_2) - (I_1 I_2)$$

I₁ = surface coverage of inhibitor (SOS)

I₂ = surface coverage of inhibitor (Zn²⁺)

I₁₊₂ = combined surface coverage of inhibitors (SOS) and (Zn²⁺)

Surface coverage = IE/100

I₂ for Zn²⁺ (5.2×10⁻⁵ mol/l) = 0.12 and I₂ for Zn²⁺ (1.04×10⁻⁴ mol/l) = 0.21

The results are given in Table 3.

Table 3 Synergism Parameter (S_I)

SOS (mol/l)	SOS- Zn ²⁺ (5.2×10 ⁻⁵)	SOS Zn ²⁺ (1.04×10 ⁻⁴)	S _I	S _I	S _I
10 ⁻³	I ₁	I ₁₊₂	S _I	I ₁₊₂	S _I
0.23	0.13	0.31	1.11	0.6	1.81
0.69	0.15	0.38	1.2	0.64	1.88
0.46	0.18	0.36	1.13	0.71	2.23
0.92	0.26	0.38	1.05	0.74	2.24
1.16	0.33	0.43	1.03	0.88	4.41

S_I Value is found to be greater than one, indicating the synergistic effect existing between Zn²⁺ of concentrations 5.2×10⁻⁵ mol/l and 1.04×10⁻⁴ mol/l with various concentrations of SOS.

3.1.3 Influence of Immersion Period on the IE of SOS (1.16×10⁻³ mol/l) - Zn²⁺(1.04×10⁻⁴ mol/l) system

The influence of immersion period on IE of SOS (1.16×10⁻³ mol/l) + Zn²⁺(1.04×10⁻⁴ mol/l) is shown in Fig.1.

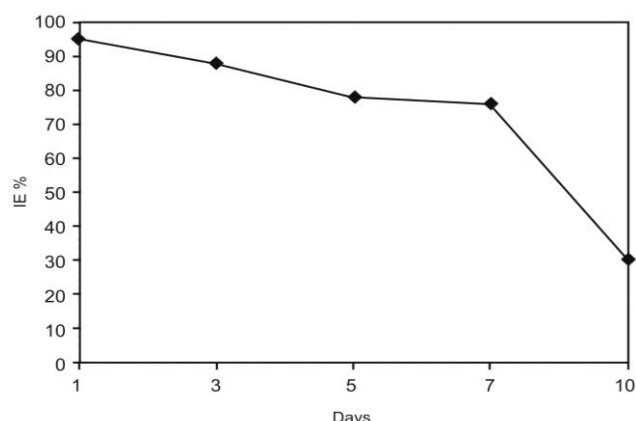


Fig.1.Influence of Immersion Period on the IE of SOS (1.16×10⁻³ mol/l) - Zn²⁺(1.04×10⁻⁴ mol/l) system

It is found that as the immersion period increases, the inhibition efficiency decreases. This may be due to the fact that, as the period of immersion increases, the protective film Fe²⁺- SOS complex, formed on the metal surface is broken by the continuous attack of other ions present in the solution and hence, the IE decreases as the immersion period increases. A similar observation has been made in the corrosion prevention of carbon steel by Methyl orange (Sathiyabama et al., 2008).

3.2. 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_c) increases and double layer capacitance (C_{dl}) value decreases (Rajendran Susai et al., 2006; Mary Anbarasi and Susai Rajendran, 2012). Nyquist representations of carbon steel in dam water in the absence and presence of the inhibitor system are shown in Fig. 2.

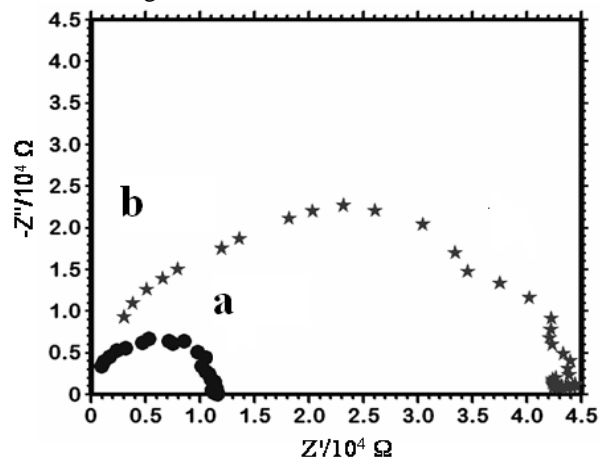


Fig. 2 AC impedance spectra of carbon steel immersed in various test solutions a) dam water b) dam water containing 1.16×10⁻³ mol/l of SOS and 1.04×10⁻⁴ mol/l of Zn²⁺

It is clear from the plots that the impedance response of carbon steel changed significantly after the addition of inhibitors. The impedance diagrams obtained have almost a semicircular appearance. This indicates that the corrosion of carbon steel in aqueous solution is mainly controlled by a charge transfer process (Grosser and Gonclaves, 2008). The deviation from the perfect semicircle shape (depression) is often referred to the frequency dispersion of interfacial impedance. This anomalous behaviour is generally attributed to the inhomogeneity of the metal surface arising from surface roughness or interfacial phenomena (Martinez and Mansfeld-Hukovic, 2003; Elayyachy et al., 2006; Shukla and Quarishi 2009). The AC impedance parameters, namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in Table 4.

Table 4 Impedance parameters of carbon steel in dam water in the presence and absence of inhibitor obtained by AC impedance method

SOS (mol/l)	Zn ²⁺ (mol/l)	R _t Ω cm ²	C _{dl} F/cm ²	Impedance log(z/ohm)
0	0	1.084×10 ⁴	8.24×10 ⁻¹⁰	4.062
1.16×10 ⁻³	1.04×10 ⁻⁴	4.1740×10 ⁴	2.17×10 ⁻¹⁰	4.643

When carbon steel is immersed in dam water, R_t value is 1.084×10⁴ Ω cm² and C_{dl} value is 8.24×10⁻¹⁰ F/cm². When SOS (1.16×10⁻³ mol/l) - Zn²⁺ (1.04×10⁻⁴ mol/l) are added to dam water, R_t value increases from 1.084×10⁴ Ω cm² to 4.1740×10⁴ Ω cm² and the C_{dl} decreases from 8.24×10⁻¹⁰ F/cm² to 2.17×10⁻¹⁰ F/cm². This suggests that a protective film is formed on the surface of the metal. This is further supported by the increase in impedance value [log(z/ohm)] from 4.062 to 4.643, (Fig.3).

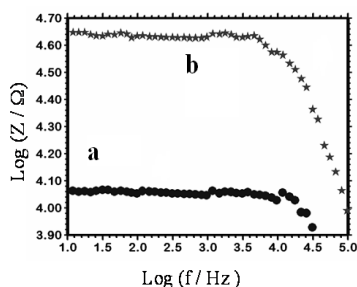


Fig. 3 AC impedance spectra of carbon steel immersed in various test solutions (Frequency Bode plots) **a)** dam water **b)** dam water containing 1.16×10⁻³ mol/l of SOS and 1.04×10⁻⁴ mol/l of Zn²⁺

This accounts for the high IE of SOS-Zn²⁺ system (Agnesia Kanimozhi and Rajendran, 2009).



Fig.4 Equivalent electrical circuit diagram

R_s = Solution resistance
 R_{ct} = Charge transfer resistance
 C_{dl} = Double layer capacitance

Results obtained from EIS measurements can be interpreted in terms of the equivalent circuit of the electrical double-layer presented in Fig. 4, which was used previously to model other interaction involving metal/solutions interface (Lebrini et al., 2008; Khaled 2008;). This type of circuit is known as Randle circuit. Many authors have also suggested Randle circuit for similar graphs (Shukla and Quarishi 2009; Prabhu et al 2008; Avci 2008).

3.3. 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 (Benita Sherine et al., 2010; Ashish Kumar Singh and Quraishi 2011; Wang et al., 2011). 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) and carbon steel surface immersed in dam water containing SOS (1.16×10⁻³ mol/l) - Zn²⁺ (1.04×10⁻⁴ mol/l) are shown in Fig.5,6 and7.

Root– mean-square roughness, average roughness and peak-to-valley value

AFM image 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) (Benita Sherine et al., 2010). Table 5 is a summary of (R_q), (R_a), (P-V) value for carbon steel surface immersed in different environment.

Table 5 AFM data for carbon steel surface immersed in inhibited and uninhibited environment

Samples	RMS(R _q) Roughness (nm)	Average(R _a) Roughness (nm)	Maximum Peak-to-valley Height (nm)
1.Polished carbon steel	4.33	3.41	35.28
2.Carbon steel immersed in dam water (blank)	31.9	24.9	420.3
3.Carbon steel immersed in dam water + SOS (1.16×10 ⁻³ mol/l) + Zn ²⁺ (1.04×10 ⁻⁴ mol/l)	0.34	0.25	23.21

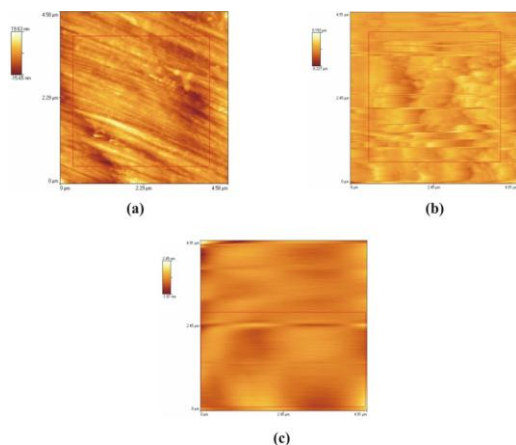


Fig. 5.Two dimensional AFM images of the surface of: a) As polished carbon steel (control); b) carbon steel immersed in dam water (blank); c) carbon steel immersed in dam water containing SO(1.16×10^{-3} mol/l) + Zn^{2+} (1.04×10^{-4} mol/l)

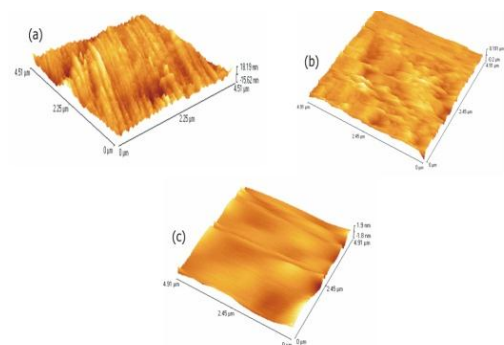


Fig.6.Three dimensional AFM images of the surface of: a) As polished carbon steel(control); b) carbon steel immersed in dam water (blank); c) carbon steel immersed in dam water containing SOS (1.16×10^{-3} mol/l) + Zn^{2+} (1.04×10^{-4} mol/l)

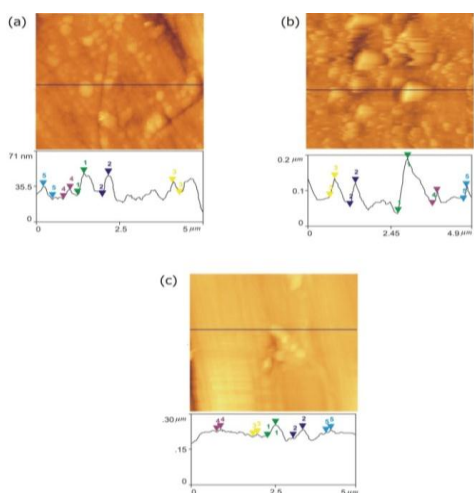


Fig.7. AFM cross-sectional images of the surface of: a) As polished carbon steel (control); b) carbon steel immersed in dam water (blank); c) carbon steel immersed in dam water containing SOS (1.16×10^{-3} mol/l) + Zn^{2+} (1.04×10^{-4} mol/l)

In image a) of figures 5, 6 and 7 the surface topography of uncorroded metal surface is shown. The value of R_q , R_a and P-V height for the polished carbon steel surface (reference sample) are 4.33nm, 3.41nm and 35.28nm respectively. The slight roughness observed on the polished carbon steel surface is due to atmospheric corrosion.

Image b) of figures 5, 6 and 7 show the pitted, corroded metal surface in the absence of the inhibitor in dam water. The (R_q), (R_a), (P-V) height values for the carbon steel surface are 31.9nm, 24.9nm and 420.3nm respectively. These data suggest that carbon steel surface immersed in dam water has greater surface roughness than the polished metal surface, which shows that the unprotected carbon steel surface is rougher and is due to the corrosion of the carbon steel in dam water environment.

Image c) of figures 5, 6 and 7 show the steel surface after immersion in dam water containing SOS (1.16×10^{-3} mol/l) - Zn^{2+} (1.04×10^{-4} mol/l). The (R_q), (R_a), (P-V) height values for the carbon steel surface are 0.34nm, 0.25nm and 23.21nm respectively. These parameters confirm that the surface is smoother. The smoothness of the surface is due to the formation of a compact protective film of Fe^{2+} - SOS complex and $Zn(OH)_2$ on the metal surface thereby inhibiting the corrosion of carbon steel (Mary Anbarasi and Susai Rajendran, 2012).

3.4. Mechanism of corrosion inhibition

With these discussions a mechanism may be proposed for the corrosion inhibition of carbon steel immersed in dam water containing SOS (1.16×10^{-3} mol/l) - Zn^{2+} (1.04×10^{-4} mol/l).When the formulation consists of SOS (1.16×10^{-3} mol/l) - Zn^{2+} (1.04×10^{-4} mol/l) in dam water there is formation of SOS – Zn^{2+} complex in the solution

1. When carbon steel is immersed in this solution SOS– Zn^{2+} complex diffuses from the bulk of the solution towards the metal surface.
2. SOS– Zn^{2+} complex is converted into SOS– Fe^{2+} complex on the anodic sites of the metal surface with the release of Zn^{2+} ion.

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

$$Zn^{2+} + 2 OH^- \rightarrow Zn(OH)_2 \downarrow$$
4. Thus the protective film consists of SOS– Fe^{2+} complex and $Zn(OH)_2$.
5. This account for the synergistic effect of SOS – Zn^{2+} system.

4. Conclusions

The present study leads to the following conclusions
 The inhibition efficiency (IE) of SOS 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 1.16×10^{-3} mol/l of SOS and 1.04×10^{-4} mol/l of Zn^{2+} has 88% IE. As the immersion period increases IE decreases. AC impedance spectra reveal that a protective film is formed on the metal surface. AFM study reveals that a compact protective film is formed on the metal surface.

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