Research Article

SYNERGISTIC AND BIOCIDAL EFFECTS OF SODIUM SACCHARIN AND ZN^{2+} SYSTEM ON THE INHIBITION OF CORROSION OF CARBON STEEL IN NEUTRAL AQUEOUS MEDIUM

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Abstract: This study is concerned with the development of new ecofriendly inhibitor system which functions efficiently in the presence of additives such as biocides for the corrosion control of carbon steel in cooling water systems. The inhibition efficiency of sodium saccharin (SS)-Zn^{2+} system in controlling corrosion of carbon steel in an aqueous environment has been evaluated by mass - loss method. A synergistic effect is noticed between sodium saccharin and Zn^{2+}. The effect of duration of immersion, influence of pH and the influence of biocides on the inhibition efficiency of the inhibitor system are studied. Polarization study and AC impedance spectral studies were carried out to find out the nature of the corrosion inhibitor The protective film formed on the metal surface has been analyzed by FT-IR, UV, SEM and AFM spectra. Based on the results obtained from the mass loss methods, polarization studies and surface analysis studies a suitable mechanism for the corrosion inhibition has been proposed.

Keywords: Corrosion inhibition, carbon steel, river water, synergistic effect

INTRODUCTION

Organic compounds containing nitrogen and sulphur have been found to function as very effective inhibitors[1-3]. As the inhibitor molecule approaches the metal surface, the electric field of double layer increases the polorization of the molecules and induces additional charges on sulphur and nitrogen atoms. This is a condition that enhances the adsorption of molecules[3-5]. Both 2-mercaptothiazoline and cetyl pyridinium chloride are effective for the inhibition of low carbon steel over a wide concentration range of aqueous phosphoric acid solution have been investigated[6].

The inhibition effect of 2-mercaptothiazoline on the corrosion behavior of mild steel in 0.5 M HCl solution in both short and long immersion times (120 h) using potentiodynamic polarization, electrochemical impedance spectroscopy and linear polarization resistance techniques have been studied[7]. The 1,2,4-triazole, 3-amino-1,2,4-triazole, benzotriazole and 2-mercaptobenzothiazole were evaluated as corrosion inhibitors for the protection of the 2024 aluminium alloy in neutral chloride solutions. The corrosion protection performance was investigated by means of DC polarization and electrochemical impedance spectroscopy[8]. The inhibitive effect of azathiones, namely cyclopentyl-tetrahydro-azathione, cyclohexyl-tetrahydro-azathione and isobutyl-methyl-tetrahydro-azathione on the corrosion of carbon steel in formic and acetic acid solution have been investigated[9]. 4-phenylthiazole derivatives as corrosion inhibitors for 304L stainless steel in 3.0 M HCl have been evaluated using weight loss and galvanostatic techniques[10].

The objectives of the present work are

- to evaluate the inhibition efficiency of sodium saccharin(SS) in controlling corrosion of carbon steel in river(namely, Cauvery in Trichy, Tamilnadu, India) water, in the presence and absence of Zn^{2+}.
- to study the biocidal efficiency of Sodium dodecyl sulphate(SDS) and N-cetyl pyridinium chloride [CPC] in the presence of the inhibitor system and their influence on the IE of SS-Zn^{2+} system.
- to analyse the protective film by FTIR.
- to make use of polarization study and AC impedance spectra to know the mechanistic aspects of corrosion inhibition.
- to analyse the film formed on the metal surface by UV absorbtion spectral studies, AFM and SEM studies.
- to propose a suitable mechanism based on the results from the above studies.

Experimental

Preparation of the carbon steel specimens

Carbon steel specimens (0.026 % S, 0.06 % P, 0.40 % Mn, 0.10 % C, and the rest iron) of dimensions 1.0 × 4.0 × 0.2 cm were polished to mirror finish, degreased with trichloroethylene and used for mass-loss and surface examination studies.

Mass- loss method

The weighed specimens in duplicate were suspended by means of glass hooks in 100 ml beakers containing 100 ml

of various test solutions. After 3 days of immersion, the specimens were taken out, washed in running water, dried and weighed. From the change in weights of the specimens, corrosion rates and I.E. were calculated.

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

Where w_1=corrosion rate(mdd) in absence of inhibitor, w_2=corrosion rate (mdd) in presence of inhibitor.

Table-1 Results of the analysis of the sample of river (The Cauvery, Tamilnadu, India) water

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S.No	Chemical Examination	Acceptable limit	Test results
1	pH	7.0-8.5	7.1
4	Total Hardness (ppm)	200-600	106
5	Ca(ppm)	150-200	21
6	Mg(ppm)	50-150	23
7	Fe(ppm)	20	0.62
8	Mn(ppm)	0.5	0.03
10	Nitrite as NO_2 (ppm)	-	0.01
11	Nitrate as NO_3(ppm)	20	0.05
12	Chloride as Cl(ppm)	200-600	254
13	Fluoride as F^-(ppm)	1	0.2
14	Sulphate as SO_4(ppm)	42-45	.08
15	P (ppm)	5	0.1
16	Total dissolved solids (mg/l)	500-1500	153

Surface examination studies

The carbon steel specimens were immersed in various test solutions for a period of three days, the specimens were taken out, washed with distilled water and then dried.The nature of the film formed on the surface of metal specimens was analysed by the following technicques.

FTIR spectra

The film was carefully removed with sharp edged glass rod, mixed thoroughly with KBr and made into pellets, and the FTIR spectra were recorded on a Perkin- Elmer 1600 spectrophotometer.

Potentiodynamic polarization study

Potentiodynamic polarization studies were carried out using CHI electrochemical impedance analyzer, model 660 A. A three-electrode cell assembly was used. The working electrode was a rectangular specimen of carbon steel with one face of the electrode (1 cm^2 area) exposed and the rest shielded with red lacquer. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode.

AC impedance measurements

A CHI electrochemical impedance analyzer (model 660 A) was used for AC impedance measurements. A time interval of 5 to 10 minutes was given for the system to attain its open-circuit potential. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms at various frequencies (f). The values of the charge transfer resistance R_t and the double layer capacitance C_{dl} were calculated.

The UV-visible absorption spectra of solutions:

The possibility of the formation of Zn- inhibitor complex and also iron-inhibitor complex in solution was examined by mixing the respective solutions and recording their UV-visible absorption spectra using Lamda 35 UV-visible spectrophotometer 119 which is a PC controlled single beam scanning spectrophotometer. It covers a wavelength range from 200 nm to 1000 nm with a setting accuracy of ± 1nm.

Atomic Force Microscopy Characterization

Atomic force microscopy is a powerful technique for the gathering of roughness statistics from a variety of surfaces. AFM is becoming an accepted method of roughness investigation. All atomic force microscopy images were obtained on a pico SPM 2100 AFM instrument operating in contact mode in air.The scan size of all the AFM images are 30μm x 30μm areas at a scan rate of 2.4 lines per second.

Scanning electron microscopy

Scaning electron microscope(SEM) Model NO 435 VP LEO was used to study the morphology of corroded surface in the presence and absence of inhibitors. The specimens were thoroughly washed with double distilled water before putting on the slide. The photographs were taken of that portion of specimen from where better information was obtained. They were photographed at 500 magnification

Biocidal efficiency

The biocidal efficiency of the system was determined using zobell medium and calculating the number of colony forming units per ml using a bacterial colony counter.

Results and Discussion
Mass-loss method

The corrosion inhibition efficiencies of sodium saccharin(SS)-Zn^{2+} systems, as determined by mass loss method, are given in Table-2. It is found from the table that SS is a poor inhibitor and 50 ppm of SS gives a maximum of 41 % IE. Perusal of the table reveals that a combination of Zn^{2+} and SS shows a better IE. For example, 50 ppm of Zn^{2+} gives an IE of 41 % and 50 ppm of SS gives 41 %, but their combination offers an IE of 90 %, which is found to be the maximum IE offered by the system. This suggests the existence of synergistic effect between Zn^{2+} and SS. The synergism may be due to the formation of complex between Zn^{2+} and SS. Because of the complex formation with Zn^{2+}

the inhibitor molecules are readily transported from the bulk to the metal surface.
On the metal surface, Zn^{2+}-SS complex is converted into Fe^{2+}- SS complex on the anodic sites of the metal surface. Zn^{2+} is released. This combines with OH^- to form $Zn(OH)_2$ on the cathodic sites of the metal surface. Thus both the anodic reaction $.Fe--------> Fe^{2+} + 2e^-$ and cathodic reaction $O_2 + 4e^- + 2H_2O---------> 4OH^-$ are controlled effectively.. This accounts for a synergistic effect between SS and $Zn^{2+.}$

Table II   Inhibition efficiency (%) offered by the inhibitor system to carbon   Steel immersed in river water

SS,			Zn^{2+},ppm		
ppm	0	5	10	25	50
0	--	13	17	32	41
10	35	29	51	66	68
25	38	32	55	71	87
50	41	46	58	79	90
75	35	36	56	74	80
100	34	35	52	70	72
125	34	35	50	68	67

Influence of duration of immersion on the IE of SS - Zn^{2+} system

It is found from Table III that the IE of the inhibitor system increases from 86 % to 90 % from the first to the third day and a slight decrease in IE is noticed on the fifth day. However, it does not decrease much after 5 days. This is attributed to the formation of a very strong and stable film on the surface of the metal that prevents the attack of oxygen, hydroxides, chlorides and other anions present in the solution.

Table III. Influence of immersion period on the inhibition efficiency of SS (50 ppm) – Zn^{2+} (50 ppm)

Immersion period,days	1	3	5	7
Inhibition efficiency,%	86	90	84	79

Influence of pH on the inhibition efficiency of SS + Zn^{2+} system

From the Table IV it is inferred that SS + Zn^{2+} system is effective in neutral solutions. However when the pH is lowered or raised, a steep fall in IE is observed. The low IE at low pH may be due to the fact that the interaction between Zn^{2+} and SS is not favorable in weakly acidic medium. At high pH Zn^{2+} ions get precipitated as $Zn(OH)_2$ resulting in the non- availability of Zn^{2+} in solution to form a complex with SS. This also proves that Zn^{2+} ion plays an important role in the inhibition process.[5]

Table IV. Influence of pH on the inhibition efficiency of SS (50 ppm) –Zn^{2+} (50 ppm).

pH		3	5	7	9	11
Inhibition efficiency, %		42	55	90	7	11

Influence of SDS and CPC on the IE of SS - Zn^{2+} system

It is understood from Table V that the inhibition efficiency of SS + Zn^{2+} system increases on the addition of 50 ppm of SDS from 90% to 96%. On further increasing the concentration of SDS, the IE increases slightly and at 100 ppm of SDS, maximum 99 % IE is achieved. The increase in IE with increase in concentration of SDS is due to the inhibitive action of Zn^{2+} + SDS system, which is found to be the maximum at critical micelle concentration.

When CPC is added to the carbon steel immersed in river water in the presence of inhibitor system, [Zn^{2+} and SS], the IE increases from 90 to 97% On further increasing the concentration of CPC, IE increases and reaches a maximum of 99 % at 100 ppm of CPC and remains constant. This clearly indicates the existence of synergism among sodium saccharin , Zn^{2+} and CPC. The synergistic combination of 50 ppm of SS, 50 ppm of Zn^{2+} and 100 ppm of CPC gives a maximum IE of 99 %.

Table V. Influence of SDS and CPC on the inhibition efficiency of the SS (500 ppm)- Zn^{2+} (50 ppm) system. Immersion period: Three days.

SS	Zn^{2+}	SDS	CR	IE	CPC	CR	IE
(ppm)	(ppm)	(ppm)	(mdd)	%	(ppm)	(mdd)	%
0	0	0	25.33	0	0	25.33	0
50	50	0	2	90	0	2	90
50	50	50	1	96	50	0.66	97
50	50	100	0.33	99	100	0.33	99
50	50	150	0.33	99	150	0.33	99
50	50	200	0.33	99	200	0.33	99
50	50	250	0.33	99	250	0.33	99
50	50	300	0.33	99	300	0.33	99

FTIR spectal analysis

The FTIR spectrum of sodium saccharin and the thin film formed on the surface of the metal after immersing in Zn^{2+} and sodium saccharin solution are shown in fig-1a &1b. The IR spectrum of sodium saccharin shows a band at 3401.3 cm^{-1}. This should be due to ν(OH) stretching motions of H_2O molecules(Nakamoto.,1986). The very strong absorbtion band at 1645cm^{-1} is due to ν(CO) stretching vibration(Günzler.,2002). The presence of strong bands at 1258 cm^{-1} and 1151 cm^{-1} are attributed to the asymmetric and symmetric ν(SO_2) stretching vibration respectively(Teleb.,2004) The band at 1457.55 cm^{-1} is due to the ν (C-N) stretching vibration of the imide. The IR spectrum of the thin film (fig-1b) shows a characteristic ν (CO) stretching at 1593 cm^{-1} and ν (C-N) stretching at 1416 cm^{-1}. The presence of a weak peak at 1230.41 cm^{-1} and at

1120.63 cm^{-1} shows the existence of sulphonyl groups in the thin film. The presence of bands of these characteristic groups clearly shows that sodium saccharin is present in the thin film. However the shift in the ν (CO) peak from 1645.71 cm^{-1} to 1593 cm^{-1} and ν (C-N) peak from 1457 cm^{-1} to 1416 cm^{-1} and ν (SO_2) peak from 1258 cm^{-1} to 1230 cm^{-1} and 1151 cm^{-1} to 1120 cm^{-1} clearly shows that these groups are involved in complex formation with metal ions. The presence of peaks at 3770 cm^{-1} and 1352.79 cm^{-1} is an indication that the film contains metal hydroxide. The peak at 3770 cm-1 may be due to the ν(OH) stretching vibration of metal hydroxide(Farmer.,1974).The peak at 1352.79 cm^{-1} is assigned to inplane bending vibration of –OH attached to metal ion and the peaks at 860 cm^{-1} and 570.72 cm^{-1} are due to M-O stretching(Powell.,1985) This shows the presence of M- OH in the film.
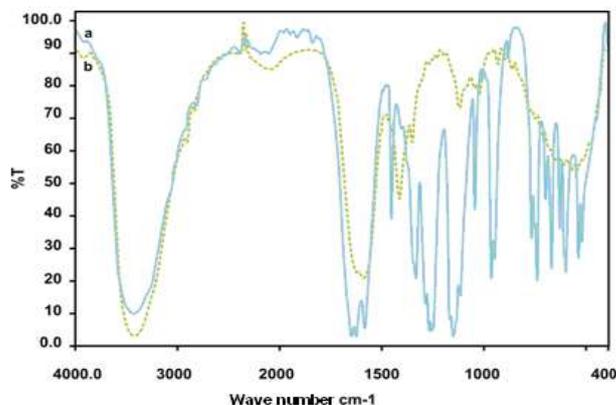

Figure :1 FTIR spectra of (a) sodium saccharin and (b) Film formed on steel after immersion in river water containing 50 ppm SS & 50ppm Zn^{2+}

Analysis of the results of potentiodynamic polarization studies:

The corrosion parameters of carbon steel immersed in cauvery water in the presence and absence of 50 ppm of Zn^{2+} and 50 ppm of SS are given in Table VI. When carbon steel is immersed in river water, the corrosion potential (E_{corr}) is -463 mV vs SCE and the corrosion current is 1.556×10^{-5} A/cm^2. When 50 ppm of Zn^{2+} and 50 ppm of sodium saccharin are added to river water the corrosion potential shifts to the cathodic side -538 mV vs SCE. The corrosion current is 0.346×10^{-5} A/cm^2. The cathodic slope

is found to change from 327 to 426 mV/ decade and the anodic slope from 217 to 171 mV/ decade. The linear polarization resistance has increased from 3.643×10^3 to 15.3×10^3 Ωcm^2. The increase in the value of b_c is considerably more than that of b_a. This shows that the formulation controls the cathodic reaction predominantly. The increase in LPR value and decrease in corrosion current indicate that a protective film is formed on the metal surface.[14]

Table VI. Electrochemical corrosion parameters for carbon steel in river water in the presence and absence of SS and Zn^{2+}.

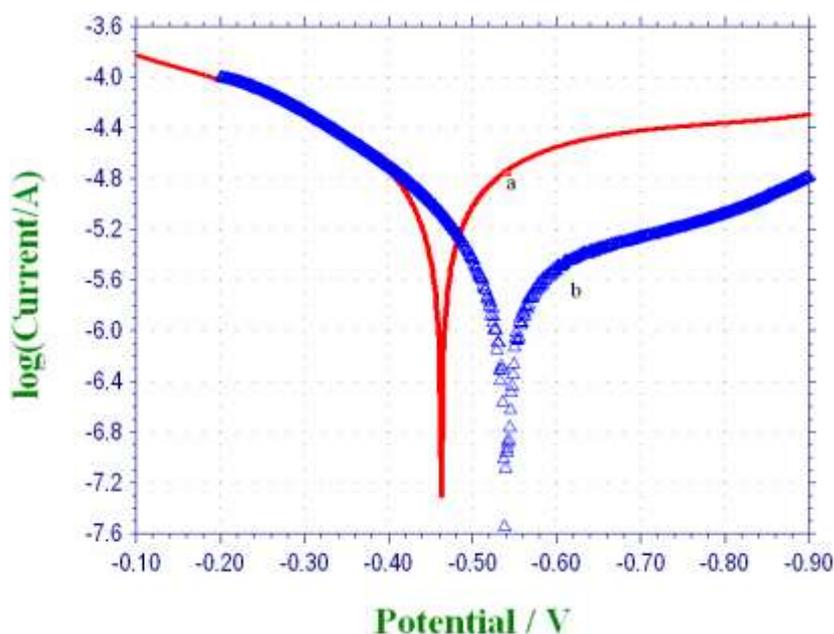| System	E_{corr} mV vs SCE	b_c mV/decade	b_a mV/decade	LPR Ω Cm^2	I_{corr} A/Cm^2
River water	-463	327	217	3.643×10^3	1.556×10^{-5}
Riverwater + 50 ppm SS + 50 ppm Zn^{2+}	-538	426	171	15.3×10^3	0.346×10^{-5}

Figure.2. Polarization curves of carbon steel immersed in river(cauvery) water and RW containing 50 ppm SS and 50 ppm Zn^{2+}

Analysis of the results of AC impedance studies:

The AC impedance spectra of carbon steel immersed in various test solutions are shown in Fig.5   The AC impedance parameters namely charge transfer resistance(Rt) and the double layer capacitance(Cdl) are given in Table VII. When carbon steel is immersed in river water the R_t value is found to be 1102 Ω cm^2. The C_{dl} value is 8.2187×10^{-9} F/cm^2. When 50 ppm of Zn^{2+} and 50 ppm of sodium

saccharin   are added the R_t value has increased from 1102 to 1662 Ωcm^2 and the C_{dl} value has decreased from 8.2187×10^{-9} to 5.4516×10^{-9} F/cm^2. The increase in R_t values and decrease in double layer capacitance values obtained from impedance studies justify the good performance of a compound as an inhibitor in river water . This behaviour means that the film obtained acts as a barrier to the

corrosion process that clearly proves the formation of the film[12-15].

When carbon steel is immersed in river water (Table-1), two semi circles are obtained (Fig-5). There are two time constants. This is characteristic of a failed coating. A less stable protective coating is formed on carbon steel, when immersed in river water. The formation of protective coating is due to the presence of various ions present in river water (Table-1). However this coating (film) degrades with time and also due to attack of corrosive ions on the film. After certain amount of time, water penetrates into the coating and forms a new liquid/ metal interface. The interpretation of impedance data from failed coatings can be very complicated. The equivalent circuit for a failed coating is shown in Fig-3.

Fig-3 Equivalent circuit for a failed coating
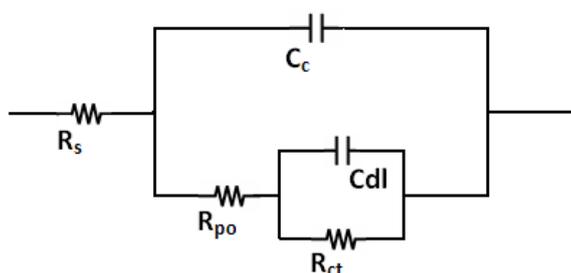
The capacitance of the intact coating is represented by Cc. Its value is much smaller than a typical double layer capacitance. Rpo (pore resistance) is the resistance of ion

conducting paths that develop in the coating. These paths may not be physical pores filled with electrolyte. On the metal side of the pore, it is assumed that an area of the coating has delaminated and a pocket filled with an electrolyte solution has formed. This electrolyte solution can be very different from the bulk solution outside of the coating. The interface between this pocket of solution and the bare metal is modeled as a double layer capacity in parallel with a kinetically controlled charge transfer reaction[16-20].

When carbon steel is immersed in river water containing 50 ppm of CP and 50 ppm of Zn^{2+} (Fig 5b), the Nyquist plot obtained is due to a combination of kinetic and diffusion process. The equivalent circuit which models a cell , where polarization is due to a combination of kinetic and diffusion process is shown in Fig-4.

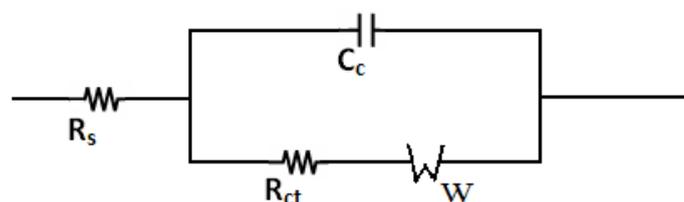**Fig -4. Equivalent circuit with mixed kinetic and diffusion control**

Table VII. Impedance parameters of carbon steel in river water in the absence and presence of inhibitor obtained by AC impedance spectra.

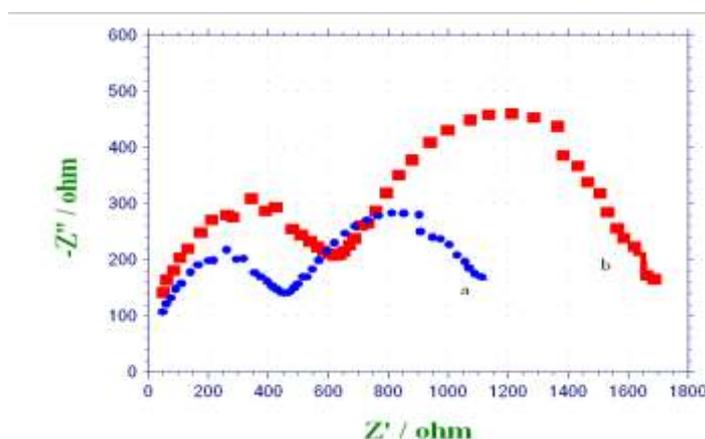| Environment	SS ppm	Zn^{2+} ppm	R_t, Ω cm^2	C_{dl} μ F/cm^2
River water	0	0	1102	$8.2187 \square 10^9$
Riverwater+ 50ppmSS+ 50ppm Zn^{2+}	50	50	1662	$5.4516 \square 10^9$

Figure-5 AC impedance spectra of carbon steel immersed in various test solutions
a) River water   b) River water + 50 ppm SS + 50 ppm Zn^{2+}
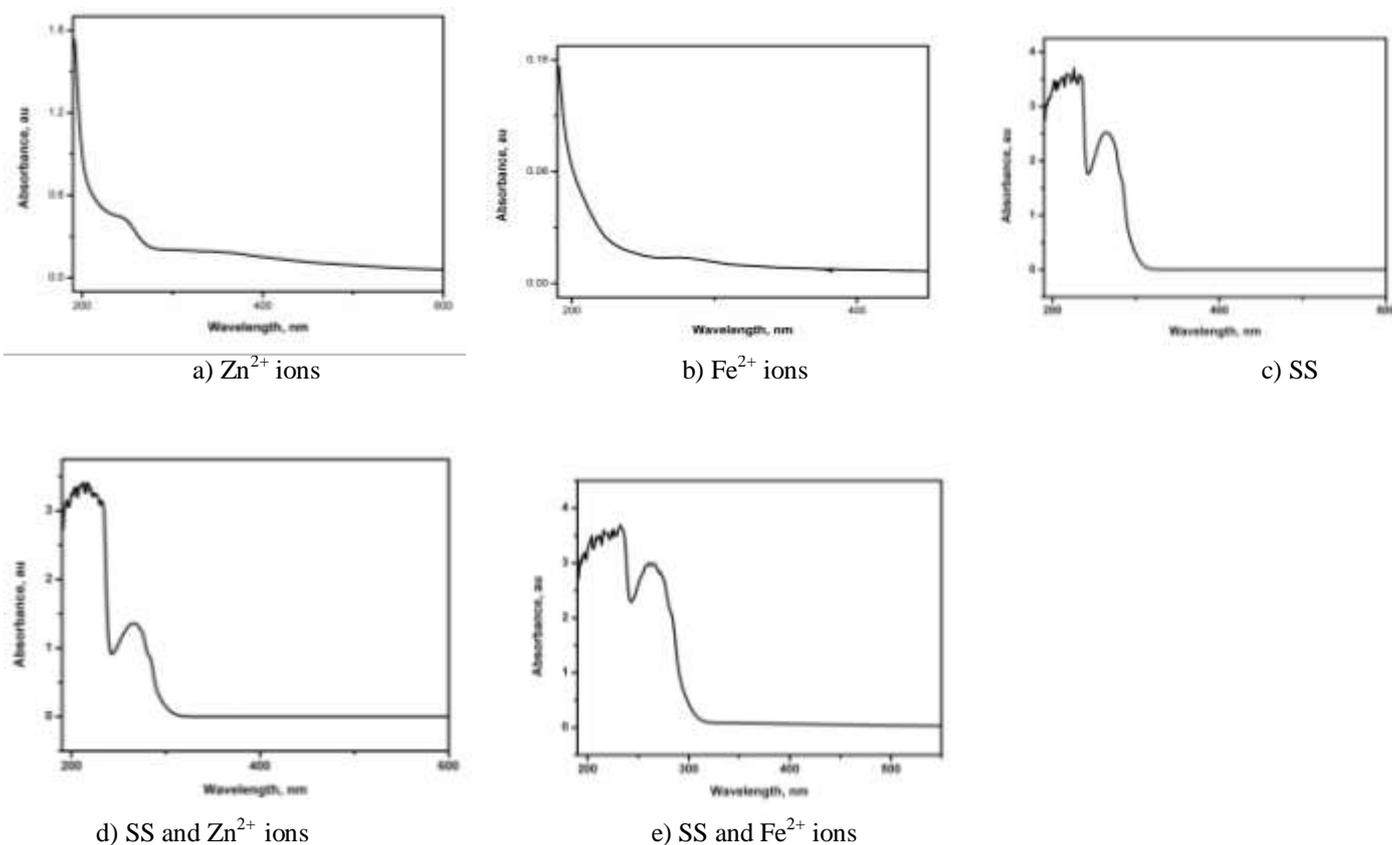
a) Zn^{2+} ions   b) Fe^{2+} ions   c) SS

d) SS and Zn^{2+} ions   e) SS and Fe^{2+} ions

Figure-6 UV-Visible absorption spectra of the test solutions in river water

UV-Visible spectral study

The UV -visible spectra of Zn^{2+}, Fe^{2+} ion, SS, Zn^{2+}- SS and Fe^{2+} - SS in distilled water are given in Fig-6a-e. The UV spectrum of sodium saccharin gives two prominent peaks (Fig-6c) at 225.98 nm (abs-3.7078) and at 264.84 nm (abs-2.5202). When Zn^{2+} ions are added to SS solution (Fig-6d) the peak at 225.98 nm is shifted to 216.18 nm (abs-3.4180) and the peak at 264.84 nm (abs-2.5202) is shifted to 266.55 nm (abs-1.3556). This shift in the peak height and the absorbance value clearly shows that there is some interaction between Zn^{2+} ion and SS. In the UV spectrum of Fe^{2+}-SS (Figure-4e) the peaks are shifted to 232.17 nm (abs-3.6859) and 264.10 nm(abs-2.9915) respectively. It is obivious from the above facts that Fe^{2+} ion also forms a complex with SS.

Analysis of atomic force micrographs

The coated protective films are examined with Atomic Force Microscope (AFM). Thetopography of all the samples for a scanned area of 5 nm x 5 nm (25 nm^2) is evaluated for a set point of 10 nA and a scan speed of 10 mm/s. The Table VII shows various AFM parameters obtained when the carbon steel surface immersed in different environments. Figure 7(a) & (b) shows one and 3D AFM images of polished metal surface. Zmax value 0.51V when compared with other thin film coated surface values indicate the absence of iron oxides on the smooth surface. Figure 7(a)& (b) shows the one and 3-D images of carbon steel immersed in river water + 50 ppm Zn^{2+}+ 50 ppm SS for 10 minutes duration respectively. When the immersion period is 10 minutes, the roughness value increases from 143.98nm to 379nm. This increased value strongly implies the formation of inhibitive film by the addition of SS additive along with the Zinc inhibitor system on the metal surface.[14]

Table VIII. AFM parameters of carbon steel immersed in neutral aqueous   environment

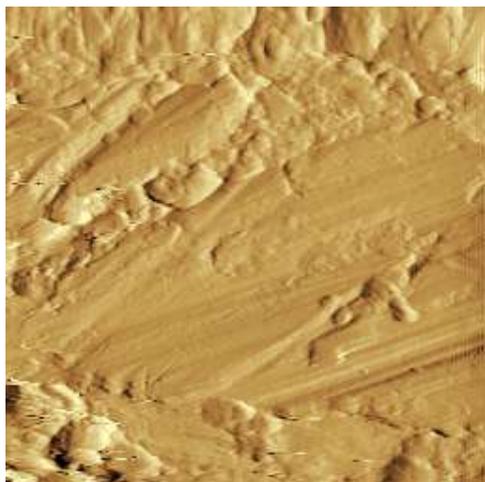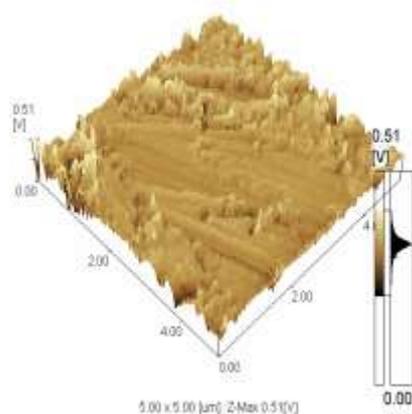| Environment	Period of immersion	AFM parameters	
		Rms nm	Zmax volts
Polished metal + river water	10 min	143.98	0.51
Polished metal + 50 ppm SS +50 ppm Zn^{2+}	10 min	379	0.78

Figure 7(a). AFM image of polished mild steel

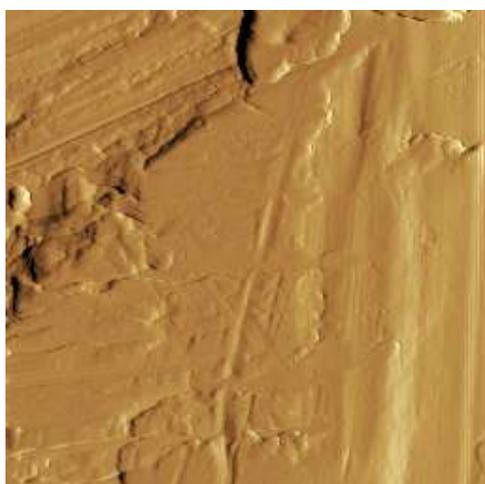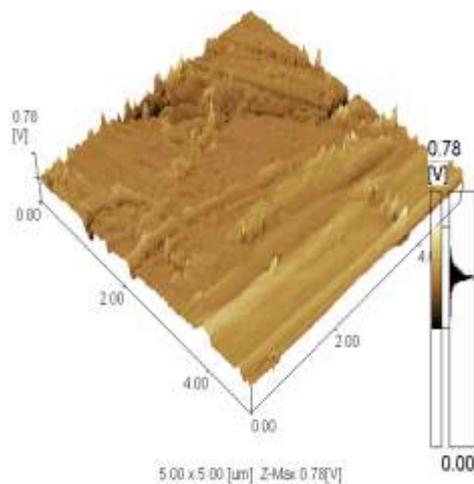**7(b).**AFM 3D image of polished mild steel surface

Figure 7(a).AFM image of polished
steel surface immersed in river water
+ 50 ppm SS

7(b). AFM 3D image of polished
mild steel in river water+ 50 ppm Zn^{2+} +50 ppm Zn^{2+}+50 ppm SS

Scanning electron microscopy (SEM)
Fig.8 shows the scanning electronic microscopy (SEM)images of ordinary steel surface that has been exposed to the simulated river water medium for three days in the absence and presence of inhibitor. The image of the surface exposed to the inhibitor-free solution (Fig.8a), shows a heterogeneous layer of products Furthermore, the SEM image of the layer formed in the presence of inhibitor (Fig.8b) shows a large area free of corrosion and scale products; hence the presence of very few corrosion products is observed. This indicates that SS is a corrosion inhibitor and an antiscalant.
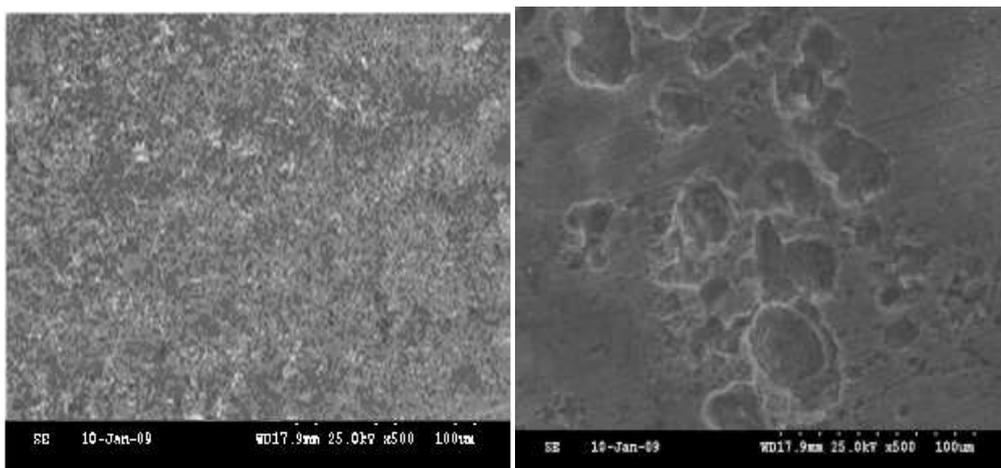
Fig.8: SEM micrographs: a) Film formed on metal surface in presence of river water, b) Film formed on metal surface in presence of riverwater + 50 ppm SS + 50 ppm Zn^{2+}

Biocidal efficiency of SDS and CPC in SS - Zn^{2+} system
Biocidal efficiencies of SDS and CPC in the presence and absence of SS -Zn^{2+} formulation after immersion of carbon steel in river water for 32hours are given in Tables IX and X. When 25 ppm of SDS is added to river water a biocidal efficiency (BE) of 92.7 % is obtained and 150 ppm of SDS offers 100 % BE. For the inhibitor system without SDS, the biocidal efficiency is found to be 47.5 % which shows that SS + Zn^{2+} combination could not control the growth of certain microbes. However when 150 ppm of SDS is added to river water in the presence of the inhibitor system, only 62 % biocidal efficiency is obtained. This may be due to the reaction between SDS and SS that results in the reduction in the concentration of both. Table X points out that CPC

offers 100 % BE when 50 ppm of CPC was added to river water in which the test specimens were immersed for 72 hours. The inhibitor formulation gives 47.5 % BE in the absence of CPC. The inhibitor formulation consisting of 50 ppm of SS, 50 ppm of Zn^{2+}ions, and 25 ppm of CPC gives 100 % BE. Therefore, a minimum of 25 ppm of CPC is required for the complete eradication of microbes. Interestingly, the same formulation offers a maximum inhibition efficiency of 99 %. As the combination of 50 ppm of SS, 50 ppm of Zn^{2+}ions and 25 ppm of CPC offer 100 % BE and 99 % IE, it is ideal to use this combination for cooling water system to control corrosion as well as microbial growth.

Table IX. Biocidal efficiencies of SDS for SS-Zn^{2+} system in river water

SS ppm	Zn^{2+} ppm	SDS ppm	Colony forming Units/ml	Biocidal efficiency %
0	0	0	1357	--
0	0	25	98	92.7
0	0	50	16	98.82
0	0	100	10	99.26
0	0	150	0	100
50	0	0	920	47.5
50	0	50	678	50
50	0	100	536	62
50	0	200	510	61

Table X. Biocidal efficiencies of CPC for SS-Zn^{2+} system in river water

SS ppm	Zn^{2+} ppm	CPC ppm	Colony forming Units/ml	Biocidal efficiency %
0	0	0	1357	--
0	0	10	5	99.63
0	0	25	2	99.85
0	0	50	0	100
50	50	0	920	47.5
50	50	10	4	99.18
50	50	25	0	100
50	50	50	0	100

Mechanism of corrosion inhibition:

❖ The analysis of the results of the mass-loss method shows that the formulation consisting of 50 ppm of sodium saccharin and 50 ppm of Zn^{2+} offers maximum IE of 90%.

❖ The AC impedance spectral studies reveal the formation of a film with higher resistance than that of the river water alone.

❖ Results of polarization study show that this formulation functions as a cathodic inhibitor.

❖ The UV – visible absorption spectra indicate the possibility of formation of iron- SS complex and also Zn^{2+} - SS complex in solution.

❖ The FTIR spectra confirm the formation of film consisting of iron - SS complex and $Zn(OH)_2$(Sekine and Hirakawa.,1986). Qualitative analysis confirms the metal hydroxide as Zinc hydroxide.

Based on the above facts the following mechanism is proposed:

❖ In river(cauvery) water containing 50ppm of Zn^{2+} and 50 ppm of sodium saccharin, a sort of complex is formed between Zn^{2+} and sodium saccharin..

❖ When the metal is immersed in this environment, this complex diffuses from the bulk of the solution to the surface of the metal.

❖ On the surface of the metal, Zn complex is converted into the iron complex at the local anodic sites, as the latter is more stable than the former.Zn-Complex + Iron $\rightarrow$ Iron – Complex + Zn^{2+}.

❖ The released Zn^{2+} ions will form $Zn(OH)_2$ in the local cathodic regions.

❖ The protective film consists of iron-complex and $Zn(OH)_2$

❖ Biocidal study reveals that this formulation has 100% B.E.

❖ The protective film formation is confirmed by Atomic force microscopic study and Scanning electron microscopic study

Acknowledgement

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