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Surface Protection of Carbon Steel by Butanesulphonic Acid–Zinc Ion System

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Abstract

Inhibition of corrosion of carbon steel in dam water by the sodium salt of butanesulphonic acid (SBS) in combination with Zinc ion (Zn^{2+}) 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. A synergistic effect exists between SBS and Zn^{2+}. Polarization study reveals that SBS-Zn^{2+} system functions as a mixed type inhibitor. These observations have been supported by surface morphology studies using Atomic Force Microscopy (AFM) studies carried out on the carbon steel samples in the absence and presence of inhibitor.

Keywords: Corrosion, carbon steel, synergistic effect, surface morphology, AFM.

Introduction

Corrosion plays a very important role in diverse fields of industry and consequently, in economics. Thus the protection of metals and alloys is of particular interest. To eliminate or to reduce these problems, water used in cooling systems is treated with inhibitive formulations. The use of organic inhibitors is one of the most widely used practical methods for protection of metals and alloys against corrosion. The efficiency of an organic compound as a corrosion inhibitor is closely associated with the chemical adsorption[1-4]. Studies report that the adsorption of organic inhibitors mainly depends on some physicochemical properties of the molecule, related to its functional groups, to the possible steric effects and electronic density of donor atoms. Adsorption is suppose also to depend on the possible interaction of p-orbitals of the inhibitor with d-orbitals of the surface atoms, which induce greater adsorption of the inhibitor molecules onto the surface of carbon steel, leading to the formation of a corrosion protectivefilm[5].

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 Armco-iron electrode in sulfuric acid has been investigated by Vracar and Drazic[6]. 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 has also been studied by Prakash Rajesh Kumar Singh and Ranju Kumar[7]. Aliev has described the influence of salts of Alkyl phenol Sulphonic acid on the corrosion of ST3 steel. The protective effect increases with temperature. The investigated compounds inhibit corrosion of ST3 steel as a result of chemical adsorption[8]. Perusal of several literatures reveals that there is no information regarding the use of SBS in combination with Zn^{2+} as corrosion inhibitor. This paper focuses on the IE of SBS in controlling corrosion of carbon steel immersed in dam water in the absence and presence of Zn^{2+}. The investigation is performed using weight loss method, polarization technique and AC impedance spectroscopy. The morphology of the protective film was examined by AFM and finally a mechanism is proposed for corrosion inhibition based on the above results.

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 which is used in cooling systems by the industries located downstream.

Material and Methods

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

Preparation of the specimen: Carbon steel specimens of size 1.0 cm × 4.0 cm × 0.2 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.

Weight-loss method: Carbon steel specimens were immersed in 100 ml of the medium containing various concentrations of the inhibitor (sodium butane 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[9]. The corrosion IE was then calculated using the equation

IE = 100 [1-(W_2/W_1)] % (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[10]

Mils penetration per year (mpy) = 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/cm^3, A = area of specimen in square inches, T = exposure time in hours.

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 polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes anodic = β_a and cathodic = β_c were calculated and linear polarization study (LPR) was done.

Atomic Force Microscopy characterization (AFM): The carbon steel specimens 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 the surface examination. Atomic force microscope (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 µm × 5 µm and the scan rate was 0.6 Hz.

Results and Discussion

Weight-loss study: The physicochemical parameters of dam water are given in table 1.

Table-1
Water analysis

Parameters	Result
Appearance	Brownish
Total dissolved solids	100 mol/l
Electrical conductivity	140 µS/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

The corrosion inhibition efficiencies of the SBS-Zn^{2+} systems and the corresponding corrosion rates of carbon steel in (mils per year) are given in table 2.

It is found that the IE increases as the concentration of SBS increases. As the concentration of Zn^{2+} increases, IE also increases. A synergistic effect exists between SBS and Zn^{2+}. For example, 250 ppm of SBS has 5%IE. 50 ppm of Zn^{2+} has 44%IE. But the formulation consisting of 250 ppm of SBS and 50 ppm of Zn^{2+} has 86%IE. i.e. the mixture of inhibitors shows better inhibition efficiency than the individual inhibitors[11].

Table-2
The corrosion inhibition efficiencies of the SBS–Zn^{2+} system and the corresponding corrosion rates of carbon steel in (mils per year)

Inhibitor SBS (ppm)	Zn^{2+}(ppm)					
	0		25		50	
	I IE (%)	CR (mpy)	IE(%)	CR(mpy)	IE(%)	CR(mpy)
0	-	4.4384	20	3.5507	44	2.4855
50	-23	5.4592	24	3.3732	52	2.1304
100	-17	5.1929	30	3.1069	68	1.4203
150	-09	4.8379	32	3.0181	72	1.2428
200	02	4.3496	34	2.9293	78	0.9764
250	05	4.2165	42	2.5743	86	0.6214

Synergism Parameter (S_I): Synergism parameters (S_I) are indications of synergistic effect existing between inhibitors. When S_I value is greater than one, synergistic effect exists between the inhibitors[12, 13]. S_I value is found to be greater than one indicating synergistic effect exists between Zn^{2+} of concentrations 25 ppm and 50 ppm with various concentrations of SBS. The results are given in table 3.

S_I=1-I_{1+2} /1-I'_{1+2} (3)

Where I_{1+2}= (I_1+I_2)-(I_1I_2), I_1=surface coverage of inhibitor (SBS), I_2=surface coverage of inhibitor (Zn^{2+}), I'_{1+2}=combined surface coverage of inhibitors (SBS) and (Zn^{2+}), surface coverage=IE %/100, I_2 for Zn^{2+} (25 ppm) =0.20 and I_2 for Zn^{2+} (50 ppm) =0.44

Table-3
Synergism parameter (S_I)

SBS (ppm)	I_1	SBS-Zn^{2+} (25 ppm) $I'_{(1+2)}$	S_I	SBS-Zn^{2+} (50 ppm) $I'_{(1+2)}$	S_I
50	-0.23	0.24	1.2947	0.52	1.4350
100	-0.17	0.30	1.3371	0.68	2.0475
150	-0.09	0.32	1.2824	0.72	2.1800
200	0.02	0.34	1.1879	0.78	2.4945
250	0.05	0.42	1.3103	0.86	3.8000

Influence of Immersion Period on the IE of SBS (250 ppm)–Zn^{2+} (50 ppm) system: The influence of immersion period on IE of SBS (250 ppm)–Zn^{2+} (50 ppm) is shown in figure1. 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 Fe^{2+}–SBS 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 carboxymethyl cellulose- Zn^{2+} system[14].

Analysis of Polarization curves: Figure 2 represents the Potentiodynamic polarization curves of carbon steel in dam water in the absence and presence of the inhibitor system. The cathodic branch represents the oxygen reduction reaction, while the anodic branch represents the iron dissolution reaction. The electrochemical parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes (β_a and β_c), and linear polarization resistance (LPR) are given in table 4. When carbon steel is immersed in dam water, the corrosion potential is –494 mV vs SCE. The formulation consisting of SBS (250 ppm)–Zn^{2+} (50 ppm) shifts the corrosion potential to –507 mV vs SCE. i.e, the corrosion potential is shifted to the cathodic side[15]. It is also observed that the shift in the anodic slope (from 166 mV/dec to 176 mV/dec) is close to the shift in the cathodic slope (from 203 mV/dec to 212 mV/dec). Hence, it can be said that the same inhibitor system functions as a mixed inhibitor. The corrosion current value and LPR value for dam water are 2.66×10^{-6} A/cm^2 and 2.053×10^4 Ω cm^2.

For the formulation of SBS (250 ppm)–Zn^{2+} (50 ppm), the corrosion current value has decreased to 3.86×10^{-7} A/cm^2, and the LPR value has increased to 1.0634×10^5 Ω cm^2. The fact that the LPR value increases with decrease in corrosion current indicates adsorption of the inhibitor on the metal surface to block the active sites and inhibit corrosion and reduce the corrosion rate[16, 17].

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[18-20]. The three dimensional (3D) AFM morphology 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 SBS (250 ppm)–Zn^{2+} (50 ppm) are shown in figure 3 and 4.

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)[18]. Table 5 is a summary of (R_q), (R_a), and (P-V) value for carbon steel surface immersed in different environment.

In image a) of figures 3 and 4 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) is 4.33 nm, 3.41 nm and 35.28 nm respectively. The slight roughness observed on the polished carbon steel surface is due to atmospheric corrosion.

Image b) of figures 3 and 4 show the pitted, corroded metal surface in the absence of the inhibitor immersed in dam water. The (R_q), (R_a), (P-V) height values for the carbon steel surface are 31.9 nm, 24.9 nm and 420.3 nm respectively. These data suggest 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 is due to the corrosion of the carbon steel in dam water environment.

Image c) of figures 3 and 4 show the steel surface after immersion in dam water containing SBS (250 ppm)–Zn^{2+} (50 ppm). The (R_q), (R_a), (P-V) height values for the carbon steel surface are 12.10 nm, 07.23 nm and 83.48 nm respectively. The

(R_q), (R_a), (P-V) height values are considerably less in the inhibited environment compared to the uninhibited environment. 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+}– SBS complex and $Zn(OH)_2$ on the metal surface thereby inhibiting the corrosion of carbon steel [18].

Mechanism of corrosion inhibition: With these discussions, a mechanism may be proposed for the corrosion inhibition of carbon steel immersed in dam water containing SBS (250 ppm)–Zn^{2+} (50 ppm).

When the formulation consists of SBS (250 ppm)–Zn^{2+} (50 ppm) in dam water, there is formation of SBS–Zn^{2+} complex in solution

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

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

Zn^{2+} –SBS + Fe^{2+} ----------> Fe^{2+} –SBS + Zn^{2+}

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

Zn^{2+} + $2OH^-$ ------------> $Zn(OH)_2$ ↓

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

This account for the synergistic effect of SBS–Zn^{2+} system.

Table-4
Corrosion parameters of carbon steel immersed in dam water in the presence and absence of inhibitor obtained by polarization method

[SBS] (ppm)	[Zn^{2+}] (ppm)	E_{corr} mV vs SCE	I_{corr} A/cm^2	β_a mV/dec	β_c mV/dec	LPR Ω cm^2
0	0	–494	2.66×10^{-6}	166	203	2.053×10^{4}
250	50	–507	3.86×10^{-7}	176	212	1.063×10^{5}

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

Samples	RMS(R_q) Roughness (nm)	Average(Ra) 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 + SBS(250 ppm)+Zn^{2+}(50 ppm)	12.10	07.23	83.48

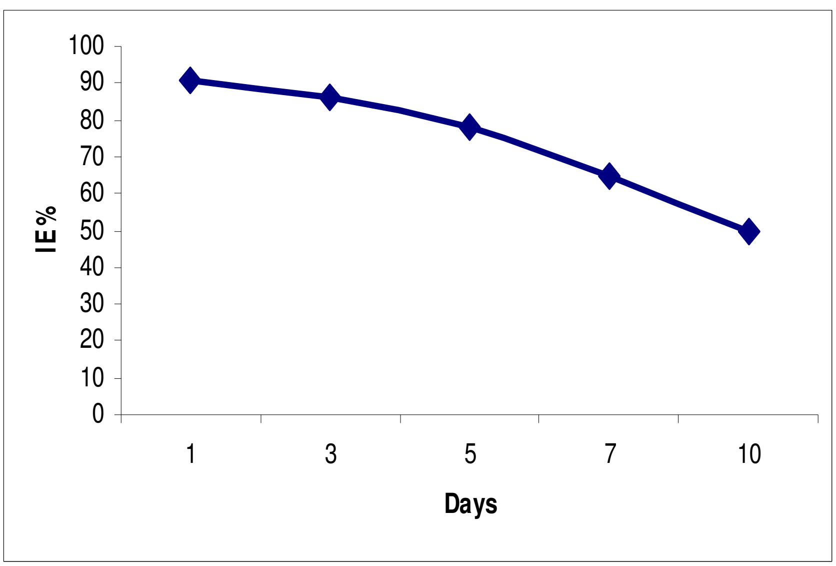


Figure-1
Influence of Immersion Period on the IE of SBS (250 ppm) - Zn^{2+} (50 ppm) system

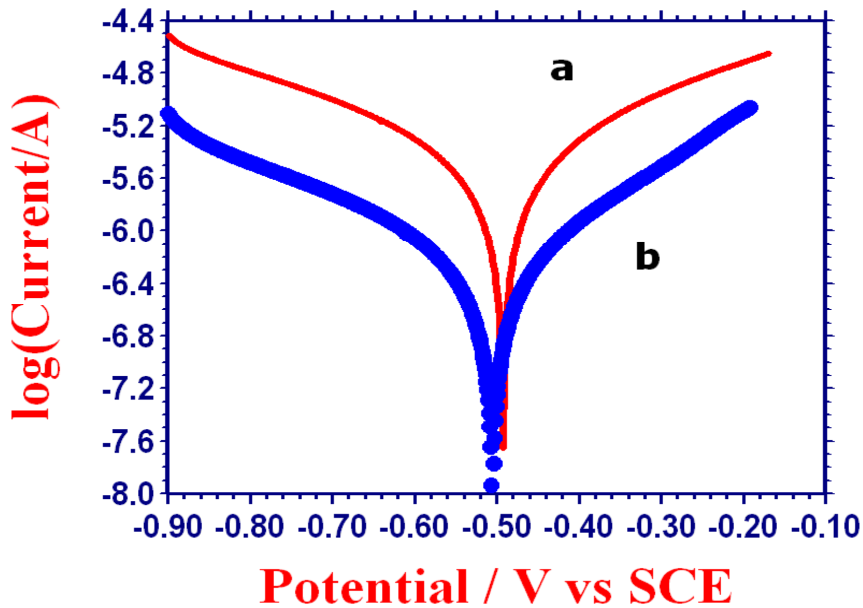
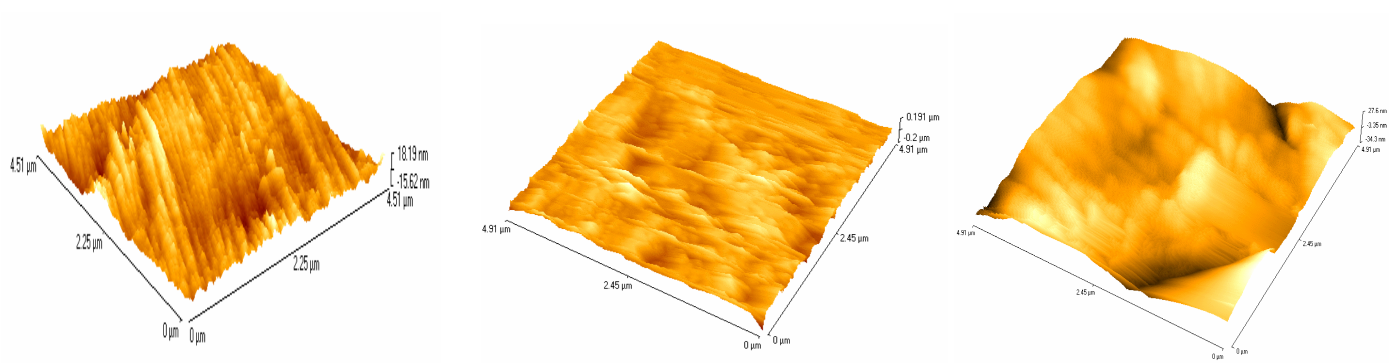
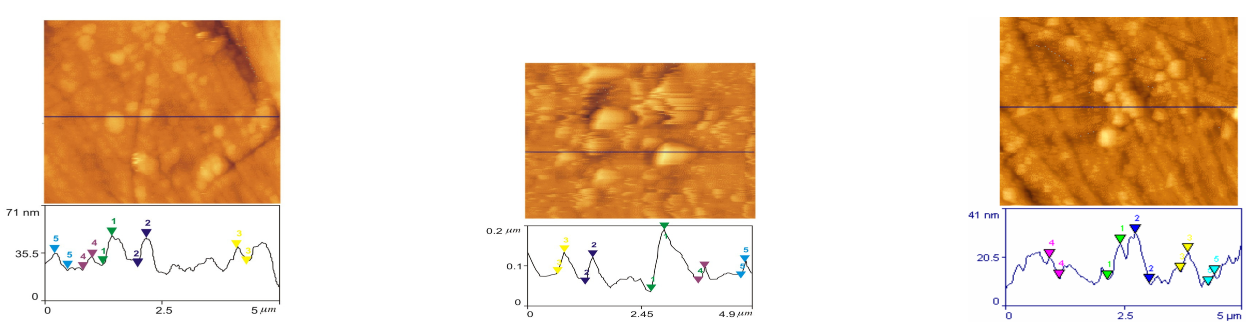


Figure-2
Polarization curves of carbon steel immersed in various test solutions (a) dam water (b) dam water containing 250 ppm of SBS and 50 ppm of Zn^{2+}



a) b) c)

Figure-3
Three dimensional AFM images of the surface of: a) polished carbon steel(control); b) carbon steel immersed in dam water (blank); c) carbon steel immersed in dam water containing SBS (250 ppm) + Zn^{2+} (50 ppm)



a) b) **c)**

Figure-4
AFM cross-sectional images of the surface of: a) polished carbon steel (control); b) carbon steel immersed in dam water (blank); c) carbon steel immersed in dam water containing SBS (250 ppm) + Zn^{2+} (50 ppm)

Conclusion

The inhibition efficiency (IE) of SBS 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 SBS and 50 ppm of Zn^{2+} has 86% IE. Polarization study reveals that SBS–Zn^{2+} system functions as a mixed type inhibitor. AFM study reveals that a compact protective film is formed on the metal surface.

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