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INHIBITIVE EFFECT OF BUTANESULPHONIC ACID-ZN²⁺ SYSTEM ON CARBON STEEL CORROSION IN AQUEOUS SOLUTION

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Abstract

This research aims to study the corrosion inhibition behaviour of butanesulphonic acid as its sodium salt C₄H₉SO₃Na (SBS) in combination with Zinc ion (Zn²⁺) on the corrosion of carbon steel in dam water using weight-loss method. Results of weight loss method indicated inhibition efficiency (IE) increased with increasing inhibitor concentration. The influence of Trisodium citrate (TSC) on the IE of the SBS-Zn²⁺ system has been evaluated. AC impedance spectra reveal that a protective film is formed on the metal surface. These observations have been supported by surface morphology studies using Fourier transform infrared spectroscopy (FTIR) and atomic force microscopy (AFM) carried out on the carbon steel samples in the absence and presence of inhibitor.

Key words: Corrosion; Carbon steel; FTIR; AFM

1. Introduction

Corrosion is a naturally occurring phenomenon which deteriorates a metallic material or its properties because of a reaction with its environment. Corrosion can cause dangerous and expensive damage to everything from pipelines, bridges and public buildings to vehicles, water and wastewater systems, and even home appliances. It is one of the most serious problems in the oil and gas industry. The use of organic inhibitors is one of the most widely 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 [1-3]. Most

well-known organic inhibitors contain nitrogen, sulfur, and oxygen atoms due to their ability to form an adsorbed protective film at the metal/ media interface. 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 supposed 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 protective film [4].

This paper focuses on the inhibition efficiency (IE) of SBS in controlling corrosion of carbon steel immersed in dam water in the absence and presence of Zn²⁺. The investigation is performed using weight loss method and AC impedance spectroscopy. The morphology of the protective film was examined by Fourier transform infrared spectroscopy (FTIR), Atomic force microscopy (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 Theni District, in the state of Tamil Nadu, India. The water from which is used in cooling systems by the industries located downstream.

2. Materials and Methods

The chemicals used in this study, sodium butane sulphonate (inhibitor) and ZnSO₄·7H₂O (Zn²⁺ ions) co inhibitor were AR grade.

2.1 Preparation of the specimen

Carbon steel specimens of size 1.0 cm × 4.0 cm × 0.2 cm, (area 10 cm²) and chemical composition 0.026 % Sulphur, 0.06 % Phosphorous, 0.4 % Manganese, 0.1 % Carbon and the rest iron (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.

2.2 Weight-loss method

Carbon steel specimens were immersed in 100 ml of the medium containing various concentrations of the inhibitor (SBS) in the absence and presence of Zn²⁺ 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) [5]. The corrosion IE was then calculated using the equation

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

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 [6]

$$\text{Mils penetration per year (mpy)} = 534 W / DAT \quad (2)$$

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

2.3 AC impedance spectra

The instrument and cell set up used for polarization study was used to record AC impedance spectra also. 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.

2.4 Surface examination study

The carbon steel specimens were immersed in various test solutions for a period of 1 day. After immersion, 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.

2.4.1 Fourier transform infrared spectra (FTIR)

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.

2.4.2 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 $5 \mu m \times 5 \mu m$ and the scan rate was 0.6 Hz.

3. Results and Discussion

3.1 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 $\mu S/cm$
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 and the corresponding corrosion rates (mils per year) of SBS- Zn^{2+} systems are given in Table 2

Table 2 The corrosion inhibition efficiencies and the corresponding corrosion rates in (mils per year) of sbs- zn^{2+} system

Inhibitor SBS (ppm)	Zn^{2+} (ppm)					
	0		15		30	
	IE(%)	CR (mpy)	IE(%)	CR(mpy)	IE(%)	CR(mpy)
0	-	4.4384	12	3.9058	21	2.5063
50	-23	5.4592	14	3.8170	42	2.5743
100	-17	5.1929	17	3.6839	49	2.2636
150	-09	4.8379	20	3.5507	53	2.0860
200	02	4.3496	22	3.4620	58	1.8641
250	05	4.2165	25	3.3288	61	1.3759

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. 30 ppm of Zn^{2+} has 21 % IE. However, interestingly, the formulation consisting of 250 ppm of SBS and 30 ppm of Zn^{2+} has 61% IE. i.e. the mixture of inhibitors shows better inhibition efficiency than the individual inhibitors [7].

3.2 Influence of Sodium potassium tartrate (TSC) on the IE of SBS (50 ppm) - Zn^{2+} (15 ppm) system

The IE and CR of carbon steel immersed in solutions containing SBS (50 ppm) - Zn^{2+} (15 ppm) and various concentrations of TSC are tabulated in Table 3.

Table 3 Influence of Trisodium citrate (TSC) on the IE of SBS (50 ppm) - Zn^{2+} (15 ppm) system

SBS (ppm)	Zn^{2+} (ppm)	TSC (ppm)	CR (mpy)	IE (%)
0	0	0	4.4384	-
50	15	0	3.8170	14
50	15	50	0.8433	81
50	15	100	0.4882	89
50	15	150	0.3551	92
50	15	200	0.6214	86
50	15	250	0.6214	86

It is noted that for TSC, IE increases up to the concentration 150 ppm and then it decreases. As the concentration of inhibitor (TSC) increases more of the inhibitor is transported towards the metal surface through the formation of Zn^{2+} -inhibitor complex. On the metal surface Zn^{2+} -inhibitor complex is converted into Fe^{2+} - inhibitor complex. This complex is insoluble, stable and more compact. So, IE increases up to 150 ppm concentration. On further increasing the concentration of the inhibitor, the complex formed on the metal surface goes into solution. So, IE decreases. Another reason may be that when more inhibitor is added, the Zn^{2+} -inhibitor complex formed is precipitated in the bulk of the solution. Also the inhibitor is not transported towards the metal surface. Hence IE decreases [8].

3.3 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_t) increases and double layer capacitance (C_{dl}) value decreases [9-11]. Nyquist representations of carbon steel in dam water in the absence and presence of the inhibitor system are shown in Fig.1.

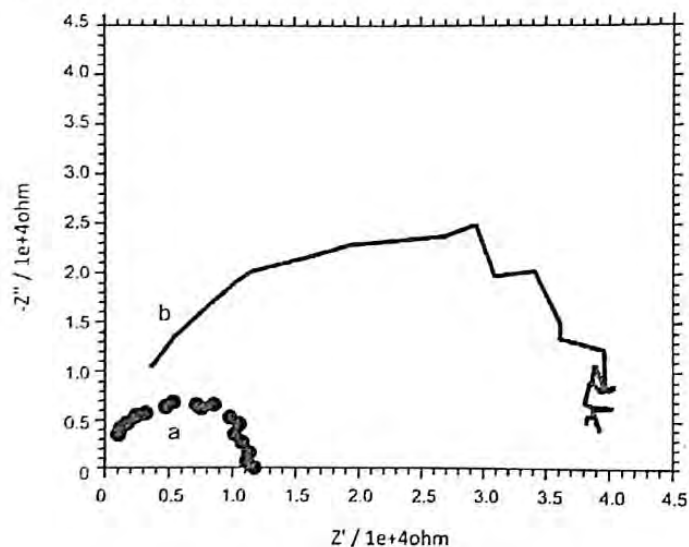


Fig.1 AC impedance spectra of carbon steel immersed in various test solutions a) dam water b) dam water containing 250 ppm of SBS and 30 ppm of Zn²⁺

It is clear from the plots that the impedance response of carbon steel was significantly changed after addition of the inhibitors. The impedance diagrams obtained have an almost semicircular appearance. This indicates that the corrosion of carbon steel in aqueous solution is mainly controlled by a charge transfer process. The deviation from the perfect semicircle shape (depression) is due to the frequency dispersion of interfacial impedance. This anomalous behavior is generally attributed to the inhomogeneity of the metal surface arising from surface roughness or interfacial phenomena [12-14]. 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

SBS (ppm)	Zn ²⁺ (ppm)	R _t Ω cm ²	C _{dl} F/cm ²
0	0	1.08×10 ⁴	8.36×10 ⁻¹⁰
250	30	3.57×10 ⁴	2.53×10 ⁻¹⁰

When carbon steel is immersed in dam water, R_t value is 1.08×10⁴ Ω cm² and C_{dl} value is 8.36×10⁻¹⁰ F/cm². When SBS (250 ppm)-Zn²⁺ (30 ppm) are added to dam water, R_t value increases from 1.08×10⁴ Ω cm² to 3.57×10⁴ Ω cm² and the C_{dl} decreases from 8.36×10⁻¹⁰ F/cm² to 2.53×10⁻¹⁰ F/cm². This suggests that a protective film is formed on the surface of the metal.

3.4 Analysis of FTIR spectra

Earlier 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 [15]. FTIR spectra have been used to analyze the protective film formed on metal surface. FTIR spectrum of pure SBS is given in Fig.2a.

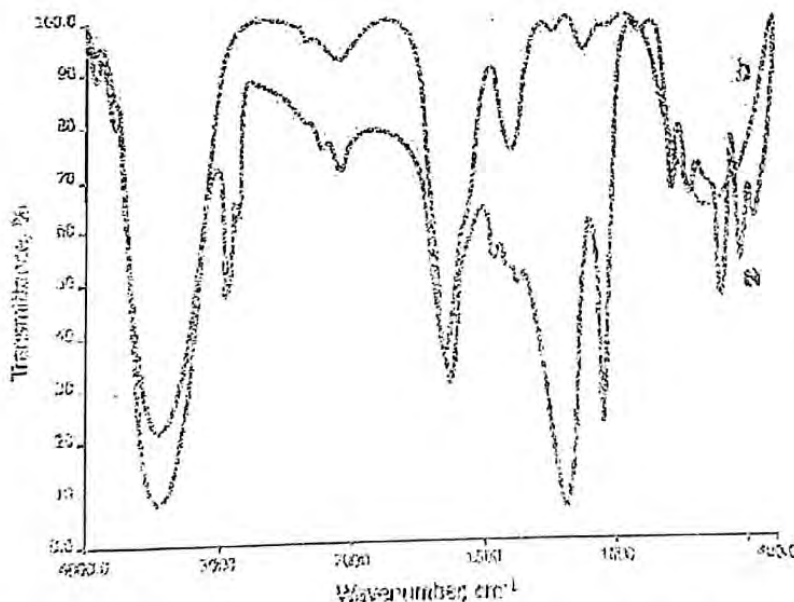


Fig.2 a) FTIR spectrum of pure sodium butane sulphonate. b) FTIR spectrum of film formed on metal surface after immersion in dam water containing 250 ppm of SBS and 30 ppm of Zn²⁺

The FTIR spectrum of the film formed on the metal surface after immersion in the dam water for one day containing 250 ppm of SBS and 30 ppm of Zn²⁺ is shown in Fig.2b The S=O stretching frequency has decreased from 1188 cm⁻¹ to 1118 cm⁻¹. This indicates that the oxygen atom of S=O group has coordinated with Fe²⁺ formed on the metal surface resulting in the formation of Fe²⁺-SBS complex on the anodic sites of the metal surface. The peak at 620 cm⁻¹ is due to Zn-O stretching. So, it is concluded that Zn (OH)₂ is formed on cathodic sites of the metal surface [16].

3.4 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 [17,18]. 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) - Zn²⁺ (30 ppm) are shown in Fig.3 and 4.

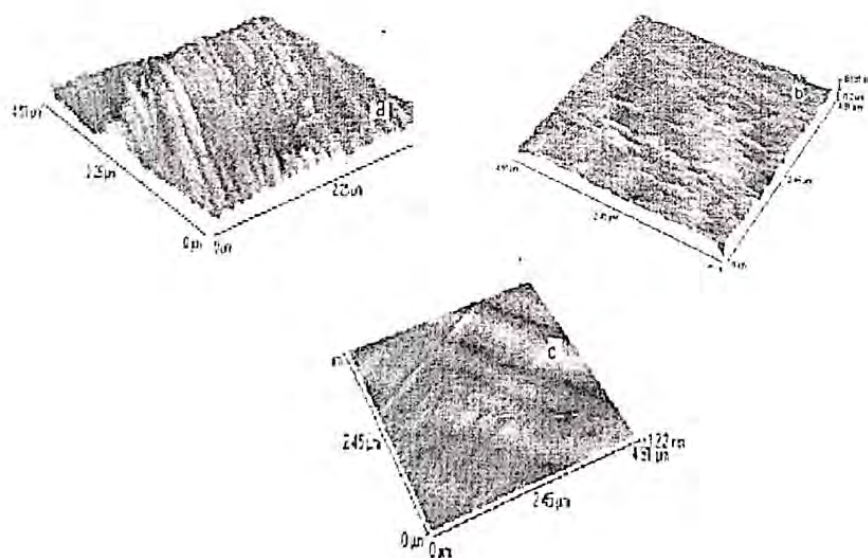


Fig.3 Three dimensional AFM images of the surface of: a) As polished carbon steel(control); b) carbon steel immersed in dam water (blank); c) carbon steel immersed in dam water containing SBS (250 ppm) + Zn²⁺ (30 ppm)

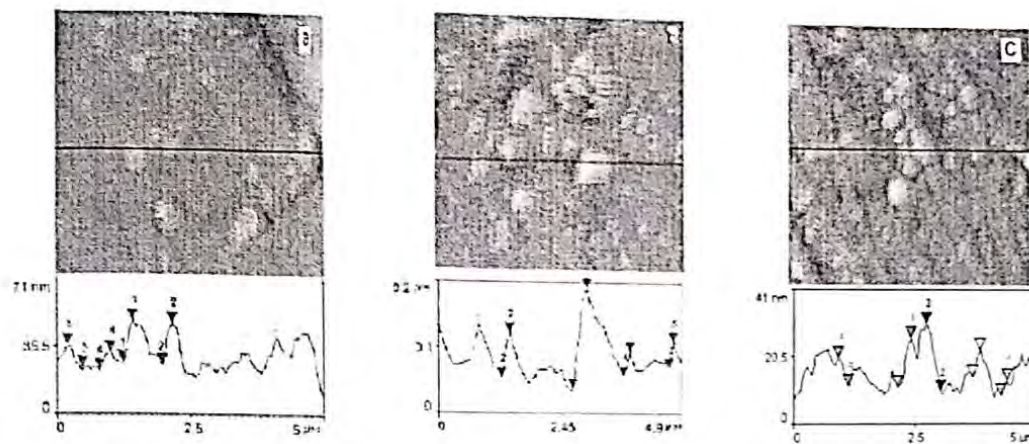


Fig.4 AFM cross-sectional images of the surface of: a) As polished carbon steel (control); b) carbon steel immersed in dam water (blank); c) carbon steel immersed in dam water containing SBS (250 ppm) + Zn²⁺ (30 ppm)

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) [19]. Table 5 is a summary of (R_q), (R_a), and (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(Roughn (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⁺ (30 ppm)	22.10	14.63	163.29

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.

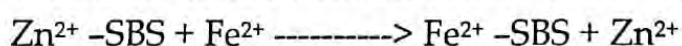
Image b) of figures 3 and 4 show the pitted, corroded metal surface in the absence of the inhibitor immersed in dam water. The (R_q), (R_a), ($P-V$) height values for the carbon steel surface are 31.9 nm, 24.9 nm and 420.3 nm respectively. These data suggest that carbon steel surface immersed in dam 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) - Zn²⁺ (30 ppm). The (R_q), (R_a), ($P-V$) height values for the carbon steel surface are 22.10 nm, 14.63 nm and 163.29 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 Fe²⁺- SBS complex and Zn(OH)₂ on the metal surface thereby inhibiting the corrosion of carbon steel [17].

3.5 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) - Zn²⁺ (30 ppm).

When the formulation consists of SBS (250 ppm) - Zn²⁺ (30 ppm) in dam water, there is formation of SBS - Zn²⁺ complex in solution

1. When carbon steel is immersed in this solution SBS- Zn²⁺ complex diffuses from the bulk of the solution towards the metal surface.
2. SBS- Zn²⁺ complex is converted into SBS- Fe²⁺ complex on the anodic sites of the metal surface with the release of Zn²⁺ ion.



The released Zn²⁺ combines with OH⁻ to form Zn(OH)₂ on the cathodic sites of the metal surface



3. Thus the protective film consists of SBS- Fe²⁺ complex and Zn(OH)₂.
4. This account for the synergistic effect of SBS - Zn²⁺ system.

4. Conclusions

The present study leads to the following conclusions. 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 30 ppm of Zn^{2+} has 61% IE. 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+} - SBS complex and $Zn(OH)_2$. AFM study reveals that a compact protective film is formed on the metal surface.

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