

Inhibition and Biocide Actions of Sodium Dodecyl Sulfate-Zn²⁺ System for the Corrosion of Carbon Steel in Chloride Solution

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Abstract

The inhibition efficiency of sodium dodecyl sulfate (SDS) in controlling corrosion of carbon steel in aqueous solution containing 120 ppm of Cl⁻ in the presence and absence of Zn²⁺ has been evaluated by weight loss method. The formulation consisting of 300 ppm of SDS and 75 ppm of Zn²⁺ gives 93 % inhibition efficiency. A synergistic effect exists between SDS and Zn²⁺. As the immersion period increases, the inhibition efficiency of SDS-Zn²⁺ decreases. Polarization study reveals that this formulation controls both the anodic and cathodic reactions. AC impedance spectra reveal that a protective film is formed on the metal surface.

Keywords: corrosion inhibitor, biocide, carbon steel, synergistic effect, SDS.

Introduction

Most of the industries require water for cooling purpose. The major problems in the industrial use of the cooling water systems are: i) corrosion of the metal equipment; ii) contamination of the circulating water with microorganisms; iii) scale formation. To solve the above problems, complex treatment of the water in the system is required. This includes addition of a) corrosion inhibitors, b) biocides, and c) antiscalants. Review of literature reveals that several surfactants that functions as corrosion inhibitors have biocidal properties [1-4]. Houyi Ma et al. [5] have investigated the inhibitive action of CTAB, SDS, sodium oleate and polyoxyethylene sorbitan monooleate on the corrosion behaviour of Cu by

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electron impedance spectroscopy. CTAB was found to be the most efficient inhibitor due to the synergistic effect between bromide anions and the positive quaternary ammonium ions. Suguna et al. [6] have determined the corrosion rates of carbon steel in the absence and presence of sodium dodecyl sulfate and Zn^{2+} in aqueous solutions. Rong Guo [7] has studied the effects of sodium dodecylsulphate (SDS) and some alcohols (ethanol / n-butanol) on the inhibition of the corrosion of Ni. Abd-El-Rehim et al. [8] have reported that the inhibition of corrosion of Al alloy in 1 M HCl in the temperature range 10-60° C occurs through the adsorption of the anionic surfactant SDS on the metal surface without modifying the mechanism of the corrosion process. The effect of SDS and Cu corrosion has been studied in the absence and presence of benzotriazole using electrochemical impedance and surface tension measurements[9,10]. Susai Rajendran et al. [11] have evaluated the inhibition efficiency of SDS in controlling the corrosion of carbon steel immersed in 60 ppm of NaCl in the absence and presence of Zn^{2+} . FTIR spectrum has revealed the presence of a film containing iron-SDS complex and $Zn(OH)_2$. Monticelli et al. [12] have investigated the corrosion inhibition of Al alloy (AA 6351) in 0.01 M NaCl using inhibitors such as sodium salts of N- dodecanoyl-N-methylglycine (NLS), dodecyl sulfate (LS), N-dodecanoyl-N- methyltaurine (NLT) and dodecylbenzene sulfonate (DBS). The existence of synergism and antagonism in mild steel corrosion inhibition by sodium dodecylbenzene sulfonate and hexamethylenetetramine has been ascribed to the formation of hemi-micellar aggregation that provokes inhibitor desorption from the metal/solution interface at higher concentration[13]. Susai Rajendran et al. [14] have reported the mutual influence of HEDP and SDS on the corrosion inhibition of carbon steel immersed in rain water in the presence of Zn^{2+} .

The present work is undertaken

- (i) to evaluate the inhibition efficiency and the biocidal efficiency of SDS - Zn^{2+} system for the corrosion of the carbon steel in 120 ppm chloride solution;
- (ii) to study the biocidal efficiency of N-cetyl-N,N,N-trimethylammonium bromide [CTAB] and N-cetyl pyridinium chloride [CPC] in the presence of the inhibitor system and their influence on the IE of SDS- Zn^{2+} system;
- (iii) to analyze the protective film on carbon steel by FTIR spectra and UV spectra;
- (iv) to understand the mechanistic aspects of corrosion inhibition by AC impedance analysis and potentiodynamic polarization studies;
- (v) to propose a suitable mechanism for corrosion inhibition.

Experimental

Preparation of the specimens

Carbon steel specimens (0.1% C, 0.026% S, 0.06% P, 0.4% Mn and the rest Fe) of dimensions 1.0×4.0×0.2 cm were polished to mirror finish and degreased with trichloroethylene.

Weight loss method

Carbon steel specimens in duplicate were immersed in 100 mL of the solutions containing various concentrations of the inhibitor in the absence and presence of Zn^{2+} for one day. The weight of the specimens before and after immersion were determined, using an ACCULAB Electronic top loading balance, with readability/sensitivity of 0.1 mg in 210 g range. The inhibition efficiency (IE) was then calculated using the equation

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

where W_1 and W_2 are the corrosion rate in the absence and in the presence of inhibitor, respectively.

Surface examination study

The carbon steel specimens were immersed in various test solutions for a period of one day. After exposure, the specimens were removed and dried. The nature of the film formed on the surface of the metal specimens was analyzed by various surface analysis techniques.

FTIR spectra

The film formed on the metal surface was carefully removed and mixed thoroughly with KBr. The FTIR spectra (KBr pellet) were recorded using a Perkin –Elmer 1600 FTIR spectrophotometer.

UV-visible spectra

The possibility of formation of Zn-inhibitor complex and also Fe^{2+} -inhibitor complex in solution was examined by mixing the respective solutions and recording their UV-visible absorption spectra, using a Systronix UV-Visible Spectrophotometer 119, which is a PC controlled single beam scanning spectrophotometer. It covers wavelength range from 200 nm to 1000 nm with a setting accuracy of ± 1 nm.

Potentiostatic polarization study

Potentiostatic polarization studies were carried out using CHI electrochemical impedance analyzer, model 6310. A three-electrode cell assembly was used. The working electrode was carbon steel. 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

The instrument used for polarization study was used for AC impedance measurements too. The cell set up was the same as that used for polarization measurements. The real part Z' and imaginary part Z'' of the cell impedance were measured in Ohms at various frequencies. The values of the charge transfer resistance R_t and the double layer capacitance C_{dl} were calculated.

Determination of biocidal efficiency of the system

The biocidal efficiency of the system was determined using Zobell medium and calculating the numbers of colony forming units per mL using a bacterial colony counter. SDS –Zn²⁺ system was selected. The biocidal efficiencies of CTAB and CPC were determined. Various concentrations of CTAB and CPC namely 50 ppm, 100 ppm, 150 ppm, 200 ppm, 250 ppm and 300 ppm, were added to the formulation consisting of the inhibitor system. Polished and degreased mild steel specimens in duplicate were immersed in these environments for a period of one day. After one day, 1 mL each of test solutions from environments was pipetted out into sterile Petri dishes, each containing about 20 mL of the sterilized Zobell medium. The Petri dishes were then kept in a sterilized environment inside the laminar flow system fabricated and supplied by CECRI-Pilani, for 48 hours. The total viable heterotropic bacterial colonies were counted using a bacterial colony counter. The corrosion inhibition efficiencies of the formulation consisting of the inhibitor in the presence of various concentrations of CTAB and CPC were also determined.

Table 1. Inhibition efficiencies (IE) of carbon steel in aqueous solution containing 120 ppm Cl⁻ in the presence of Zn²⁺ obtained by the weight loss method. Inhibitor: SDS + Zn²⁺.

SDS (ppm)	Inhibition efficiency (IE)% , Zn ²⁺ (ppm)					
	0	10	25	50	75	100
0	0	15	19	26	30	40
50	29	44	40	65	73	50
100	12	29	48	71	84	60
150	5	13	58	73	87	63
200	-1	10	59	78	88	69
250	-17	7	66	79	92	90
300	-17	7	66	79	92	90

Results and discussions**Analysis of results of weight loss method**

The corrosion rates of carbon steel immersed in 120 ppm of Cl⁻ in the presence and absence of inhibitor systems and inhibition efficiencies are given in Tables 1 and 2.

When carbon steel was immersed in aqueous environment containing 120 ppm of Cl⁻, the corrosion rate was 39.00 mdd. Upon addition of various concentrations of SDS, the corrosion rate increased. There was protection of the metal from corrosion when 300 ppm of SDS and 75 ppm Zn²⁺ were added, offering a maximum of 93% inhibition efficiency.

Table 2. Corrosion rates (CR) of carbon steel in aqueous solution containing 120 ppm Cl⁻ in presence of Zn²⁺ obtained by weight loss method. Inhibitor: SDS + Zn²⁺.

SDS (ppm)	Corrosion rate (CR) mdd					
	0	10	25	50	75	100
0		33.15	31.59	28.86	27.30	23.40
50		21.70	23.21	13.63	10.35	19.31
100		27.73	20.40	11.27	6.19	15.64
150		33.90	16.52	10.65	5.16	14.42
200		35.27	16.08	8.44	4.81	12.09
250		36.17	13.08	8.37	3.26	3.72
300		33.06	18.09	6.26	2.73	3.51

Influence of Zn²⁺ on the inhibition efficiency of SDS

The influence of a divalent metal ion Zn²⁺, on the inhibition efficiency of SDS in controlling corrosion of carbon steel, is given in Table 1. The inhibition efficiencies of various concentrations of Zn²⁺, namely 10, 25, 50, 75 and 100 ppm were 15, 19, 26, 30 and 40%, respectively. It is seen from Table 1 that at 10 ppm of Zn²⁺ there is a decrease in the IE of the SDS system. This may be due to the fact that SDS is not transported towards the metal surface, i.e., SDS- Zn²⁺ complex is precipitated in the bulk of the solution. In the presence of higher concentration of Zn²⁺ (75 ppm) the IE increases (Table 2). For example 300 ppm of SDS has 93% IE in the presence of 75 ppm of Zn²⁺. This suggests that a synergism exists between Zn²⁺ and SDS [15-17].

Influence of duration of immersion on the IE of SDS - Zn²⁺ system

As the duration of immersion increases the IE decreases (Table 3). This may be due to the fact that, as the period of immersion increases, the protective film formed on the metal surface, namely, Fe²⁺-SDS complex, is broken by the aggressive chloride ions present in the solution. Hence there is a competition between formation of FeCl₂ (and also FeCl₃) and the formation of Fe²⁺-SDS complex. As the immersion period increases, the formation of FeCl₂ is more favoured than the formation of Fe²⁺-SDS complex at the anodic sites of the metal. Hence, a decrease in the IE is noticed as the period of immersion increases [18].

Table 3. Influence of immersion period on the inhibition efficiency of SDS (300 ppm) – Zn²⁺ (75 ppm).

Days	1	3	5	7
Inhibition efficiency (%)	93	78	70	38

Influence of pH on the IE of SDS - Zn²⁺ system

At pH 5 the system shows 98% IE (Table 4). In the acidic medium (addition of dil.H₂SO₄) better inhibition efficiency is observed. But in the basic medium, i.e., above pH 7, a sudden increase in CR is noticed. This is due to the fact that in the basic medium, Zn²⁺ is precipitated as Zn(OH)₂. As Zn²⁺ ions are responsible for the transport of inhibitor to the metal surface, the amount of inhibitor transported to the metal surface is reduced and hence the increase in CR is noticed [19].

Table 4. Influence of pH on the inhibition efficiency of SDS (300 ppm) –Zn²⁺ (75 ppm).

pH	5	7	9	11
Inhibition efficiency (%)	98	93	11	1

Table 5. Influence of CTAB and CPC on the inhibition efficiency of the SDS (300 ppm)- Zn²⁺ (75 ppm) system. Inhibitor system: SDS, Zn²⁺, CTAB and CPC. Immersion period: one day.

Zn ²⁺ (ppm)	SDS (ppm)	CTAB (ppm)	CR (mdd)	IE (%)	CPC (ppm)	CR (mdd)	IE (%)
0	0	0	39.00	-	0	39.00	-
75	300	0	2.73	93	0	2.73	93
75	300	50	4.06	90	50	3.87	90
75	300	100	9.28	76	100	8.92	77
75	300	150	10.07	74	150	9.38	76
75	300	200	7.84	80	200	10.46	73
75	300	250	6.53	83	250	10.55	73
75	300	300	6.53	83	300	13.74	65

Influence of CTAB and CPC on the IE of SDS - Zn²⁺ system

The CR of carbon steel immersed in Cl⁻ ion solution containing Zn²⁺-SDS inhibitor formulation for various concentrations of CTAB and CPC and the inhibition efficiencies are tabulated in Tables 5 and 6, respectively. From Table 5 it is noted that the IE decreases with the increase in the concentration of CTAB up to 150 ppm beyond which an increase in IE is observed. The decrease in IE is due to the formation of precipitate on the addition of CTAB. The increase in IE above 150 ppm of CTAB may be due to the corrosion inhibition property of CTAB with Zn²⁺ [20]. It is observed from the Table 6 that the IE of SDS –Zn²⁺ system is reduced from 93 % to 65%, on the addition of the surfactant CPC. This

is due to the precipitation of SDS that occurs as a result of the interaction between CPC and SDS.

Table 6. Electrochemical corrosion parameters for carbon steel in chloride solution in presence and absence of SDS and Zn^{2+} .

Inhibitor system	E_{corr} mV vs. SCE	b_c mV/decade	b_a mV/decade	R_p $\Omega\text{ cm}^2$	I_{corr} A/cm ²
Chloride solution(120 ppm)	-505	464	224	8.113×10^2	8.090×10^{-5}
Chloride solution(120 ppm) +SDS (300 ppm)+ Zn^{2+} (75 ppm)	-500	368	231	9.706×10^2	6.361×10^{-5}

Analysis of FTIR spectra

FTIR spectra (KBr) of pure SDS are shown in Fig.1a . The peaks at 2854.13 cm^{-1} and 2921.63 cm^{-1} are due to the aliphatic -C-H stretching frequency. -S=O stretching frequency appears at 1222.65 cm^{-1} .and -S-O stretching frequency occurs at 588.18 cm^{-1} . The peaks due to -S-O-C- appear at 995.09 cm^{-1} and 831.17 cm^{-1} . The bands at 1471.42 cm^{-1} , 1375.00 cm^{-1} and 717.39 cm^{-1} are due to bending -C-H of methyl and methylene groups. The band at 1079.94 cm^{-1} represents the characteristic group frequency of SO_4^{2-} group [21].

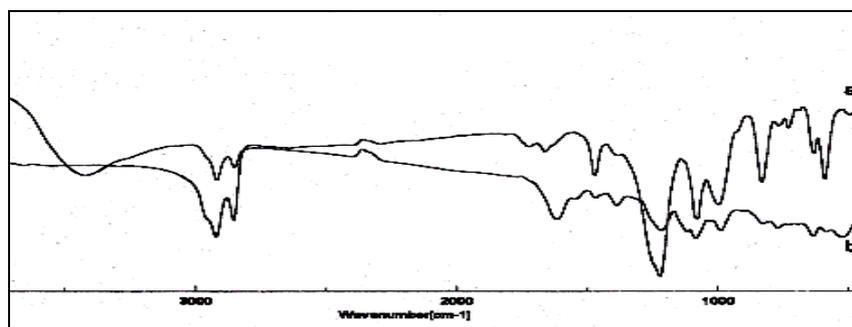


Figure 1. FTIR spectra of (a) pure SDS and (b) film formed on the surface of the carbon steel immersed in chloride ion solution containing SDS and Zn^{2+} .

The FTIR spectrum (KBr) of the film formed on the surface of the carbon steel after immersion in the solution containing 120 ppm of Cl^{-} ion , 75 ppm of Zn^{2+} and 300 ppm of SDS is shown in Fig. 1b. The -S-O stretching frequency has decreased from 1222.65 to 1213.01 cm^{-1} . ν_{S-O} has shifted from 588.18 cm^{-1} to 576.61 cm^{-1} . The bands due to S-O-C are shifted from 995.09 cm^{-1} and 831.17 cm^{-1} to 983.52 cm^{-1} and 827.31 cm^{-1} , respectively. These shifts indicate that the e^{-} clouds of -S=O and -S-O are shifted towards Fe^{2+} resulting in the formation of Fe^{2+} -SDS complex on the metal surface [11]. The bands at 777.17 cm^{-1} and 894.81 cm^{-1} may be due to Zn-O bending vibration and stretching frequency, respectively [22]. The band at 522.61 cm^{-1} may be due to Fe-O stretching vibration [23].

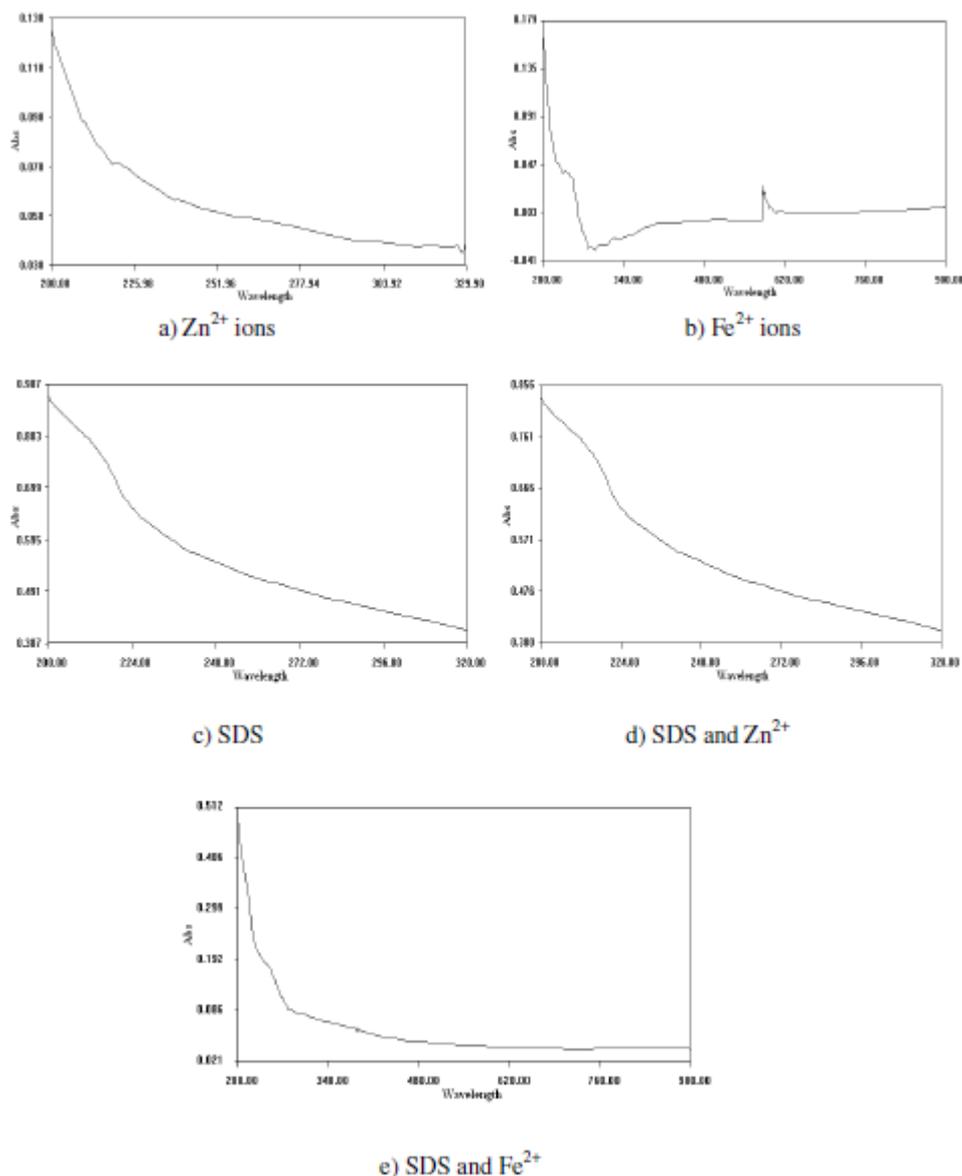


Figure 2. UV-visible absorption spectra of the test solutions in DD water.

Analysis of UV-visible spectra

The UV -visible spectra of Zn^{2+} ions, Fe^{2+} ions, SDS, Zn^{2+} -SDS, and Fe^{2+} -SDS in 120 ppm of Cl^- solution are given in Fig. 2a-e. From Fig. 2c, it is observed that the absorbance of the solution containing 300 ppm of SDS is 0.883 at 200 nm and it decreases with increase in λ and reaches a value of 0.413 at 319 nm. Fig. 2a shows that the absorbance of 75 ppm of Zn^{2+} is 0.126 at 200 nm and it decreases with increase in λ , and reaches 0.038 at 329 nm. It is evident from Fig. 2d that the addition of 75 ppm of Zn^{2+} to a solution of 300 ppm of SDS decreases the absorbance value from 883 to 835 at 200 nm, and it reaches 0.403 at 319 nm. This clearly indicates the existence of interaction between Zn^{2+} and SDS. From Fig. 2b it is noted that Fe^{2+} gives an absorbance of 0.169 at 200 nm. When Fe^{2+} ions are added to 300 ppm of SDS, the absorbance changes to 0.488 at 200 nm and reaches 0.005 at 897 nm (Fig. 2e). The change in absorbance value indicates the occurrence of reaction between Fe^{2+} with SDS.

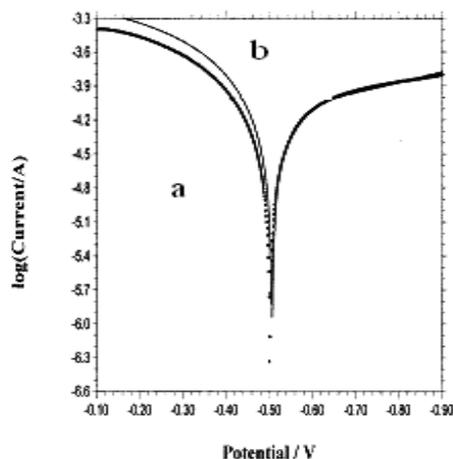


Figure 3. Polarization curves of carbon steel immersed in various test solutions. (a) Cl^- (120 ppm) in DD water, (b) Cl^- (120 ppm) + Zn^{2+} (75 ppm) + SDS (300 ppm) in DD water.

Analysis of polarization curves

The potentiodynamic polarization curves of carbon steel immersed in aqueous solution containing 120 ppm Cl^- are shown in Fig. 3. The corrosion parameters are given in Table 6.

When carbon steel is immersed in aqueous solution containing 120 ppm Cl^- , the corrosion potential (E_{corr}) is -505 mV vs. SCE. When 75 ppm of Zn^{2+} and 300 ppm of SDS are added to the above system, the corrosion potential shifted to anodic side (-500 mV vs. SCE). As there is not much change in the corrosion potential value, it is concluded that the inhibitor system behaves as a mixed inhibitor and this formation controls the anodic reaction predominantly. The corrosion current is $8.090 \times 10^{-5} \text{ A/cm}^2$ when carbon steel is immersed in chloride ion solution and it decreases to $6.361 \times 10^{-5} \text{ A/cm}^2$ when immersed along with inhibitor formulation. This suggests the inhibitive nature of this inhibitor system. The cathodic slope is found to change from 464 to 368 mV/decade and the anodic slope from 224 to 231 mV/decade. The linear polarization resistance has increased from 8.113×10^2 to $9.706 \times 10^2 \text{ } \Omega \text{ cm}^2$. This shows that the formulation functions as mixed inhibitor, controlling both anodic and cathodic processes, but predominantly the cathodic one [24-27]. Higher polarization of anode at low current densities indicates film formation at anodic sites. This infers that the protective effect of SDS appears to be due to the formation of an insoluble SDS- Zn^{2+} film. Hence the mechanism of inhibition is due to the blockage of the anodic sites first by adsorption which enables the formation of a protective insoluble film [28].

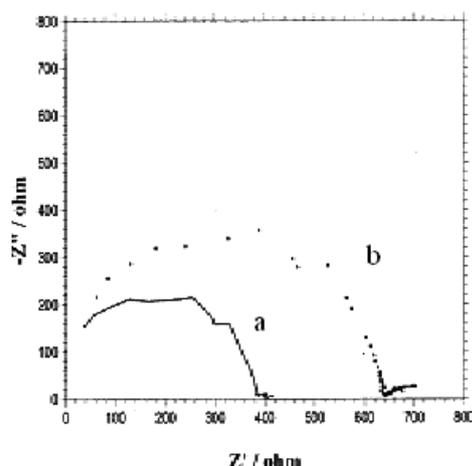


Figure 4. AC impedance of carbon steel immersed in various test solutions: (a) Cl^- (120 ppm) in DD water; (b) Cl^- (120 ppm) + Zn^{2+} (75 ppm) + SDS (300 ppm) in DD water.

Analysis of the AC Impedance Spectra

The AC impedance spectra of carbon steel immersed in aqueous solution containing 120 ppm Cl^- in the presence and absence of inhibitors are shown in Fig. 4. The AC impedance parameters namely charge transfer resistance and the double layer capacitance are given in Table 7. It is found that, when carbon steel is immersed in 120 ppm Cl^- , the R_t value is $352.02 \Omega \text{ cm}^2$ and the C_{dl} value is $1.4475 \times 10^{-8} \mu \text{ F/cm}^2$. When 75 ppm of Zn^{2+} and 300 ppm of SDS have been added, the R_t value has increased from $352.02 \Omega \text{ cm}^2$ to $581.67 \Omega \text{ cm}^2$ and the C_{dl} value decreases from $1.4475 \times 10^{-8} \mu \text{ F/cm}^2$ to $0.8760 \times 10^{-8} \mu \text{ F/cm}^2$. This behavior means that the film obtained acts as a barrier to the corrosion process that clearly proves the formation of the film [29].

Table 7. AC impedance measurements for carbon steel in chloride solution in presence and absence of SDS- Zn^{2+} system.

Inhibitor system	$R_t \Omega \text{ cm}^2$	$C_{dl} \mu \text{ F/cm}^2$
Chloride solution (120ppm)	352.02	1.4475×10^{-8}
Chloride solution (120 ppm)+SDS (300 ppm) + Zn^{2+} (75 ppm)	581.67	0.8760×10^{-8}

Biocidal efficiency of CTAB and CPC in SDS - Zn^{2+} system

Biocidal efficiencies of CTAB and CPC in the presence and absence of SDS - Zn^{2+} formulation after immersion of carbon steel in 120 ppm Cl^- solution for 24 hours are given in Tables 8 and 9. It is seen from Table 8 that 10 ppm of SDS alone in chloride ions solution show biocidal efficiency of 19 %. Increase in the concentration of SDS increases the BE and 100 ppm of SDS give 100 % BE. This clearly indicates that SDS itself is acting as a biocide. Table 9 shows that the addition of CTAB does not alter the biocidal efficiency of SDS and the biocidal nature of CTAB is well known [30]. Table 9 shows that 25 ppm of CPC

alone are sufficient to achieve 100 % BE for 120 ppm of chloride solution. However, when 100 ppm of CPC are added to the SDS-Zn²⁺ system the biocidal efficiency decreases. This may be due to the reaction between SDS and CPC that results in the reduction in the concentration of both. It is also evident from the table that even in the absence of CTAB or CPC, the inhibitor formulation offers 100 % BE. This suggests that SDS alone can act as biocide.

Table 8. Biocidal efficiencies of CTAB for SDS-Zn²⁺ system in 120 ppm of chloride solution.

Cl ⁻ ppm	SDS ppm	Zn ²⁺ ppm	CTAB ppm	Colony forming units/mL	Biocidal efficiency %
120	0	0	0	1474	--
120	0	0	10	7	99.52
120	0	0	25	0	100
120	0	0	50	0	100
120	10	0	0	1200	19
120	50	0	0	3	99.80
120	100	0	0	0	100
120	300	75	0	0	100
120	300	75	10	0	100
120	300	75	50	0	100
120	300	75	100	0	100
120	300	75	150	0	100

Table 9. Biocidal efficiencies of CPC for SDS-Zn²⁺ system in 120 ppm of chloride solution.

Cl ⁻ ppm	SDS ppm	Zn ²⁺ ppm	CPC ppm	Colony forming units/mL	Biocidal efficiency %
120	0	0	0	1474	--
120	0	0	10	3	99.80
120	0	0	25	0	100
120	0	0	50	0	100
120	10	0	0	1200	19
120	50	0	0	3	99.80
120	100	0	0	0	100
120	300	75	0	0	100
120	300	75	10	0	100
120	300	75	50	0	100
120	300	75	100	2	99.86
120	300	75	150	1	99.93
120	300	75	200	0	100

Mechanism of corrosion inhibition

Weight loss study reveals that the formulation consisting of 120 ppm Cl⁻, 300 ppm of SDS and 75 ppm of Zn²⁺ offers 93 % IE to carbon steel immersed in aqueous solution containing 120 ppm Cl⁻. A synergistic effect exists between SDS- Zn²⁺. Polarization study reveals that this formulation behaves as a mixed inhibitor. AC impedance spectra reveal that the protective film is formed on the metal surface. FTIR spectra reveal that the protective film consists of SDS- Zn²⁺ and Zn(OH)₂.

In order to explain the above facts in a holistic way the following mechanism of corrosion inhibition is proposed:

- when the formulation consisting of 120 ppm Cl^- , 300 ppm of SDS and 75 ppm of Zn^{2+} is prepared, there is formation of Zn^{2+} -SDS complex in solution;
- when carbon steel is immersed in the solution, the Zn^{2+} -SDS diffuses from the bulk of the solution towards the metal surface;
- on the metal surface, Zn^{2+} -SDS complex is converted to Fe^{2+} -SDS complex, and Zn^{2+} is released;
- the released Zn^{2+} combines with OH^- to form $\text{Zn}(\text{OH})_2$ on the cathodic sites
 $\text{Zn}^{2+} + \text{OH}^- \rightarrow \text{Zn}(\text{OH})_2$
- thus the protective film consists of Zn^{2+} -SDS complex and $\text{Zn}(\text{OH})_2$. This accounts for the synergistic effect.

Conclusions

The present study leads to the following conclusions:

- the formulation consisting of 120 ppm Cl^- , 300 ppm of SDS and 75 ppm of Zn^{2+} offers 93 % IE to carbon steel immersed in aqueous solution containing 120 ppm Cl^- ;
- a synergistic effect exists between SDS and Zn^{2+} ;
- polarization study reveals that this formulation behaves as mixed inhibitor controlling both the anodic and cathodic reactions;
- AC impedance spectra and FTIR spectra reveal that a protective film is formed on the metal surface.

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