

Corrosion Studies of Zinc Coated Steel Parts in Sea Water

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Abstract

The corrosion inhibition of zinc coated steel sheets immersed in 3.5% NaCl with sulfisoxazole (SSZ) has been reported by weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy, hydrogen permeation studies and quantum mechanical studies. All these techniques indicate that SSZ significantly inhibits zinc coated steel corrosion in a 3.5% NaCl medium. Polarization studies confirmed that the inhibition mode follows a mixed type. The adsorption of the compounds onto the zinc coated steel surface obeyed Langmuir adsorption isotherm.

Keywords: antibiotics, hydrogen permeation, corrosion inhibitors, non-toxic.

Introduction

Zinc coated steel is widely used in applications such as buildings, automotive metal parts and water pipeline systems, because of its excellent corrosion resistance to moisture [1-6]. However, failure of zinc coated pipes and tanks has been reported to be due to corrosion processes in chloride environments, which is evident from the formation of rust in those systems, leading to severe damage of industrial components. [7].

Numerous reports on zinc coated steel corrosion resistance to acidic media are available, but the use of inhibitors is an important one [8-10].

The usage of inhibitors is inexpensive and a real method to reduce electrochemical corrosion. Numerous organic compounds which have π bonds and contain hetero atoms were reported as corrosion inhibitors by several investigators [11-16], for the dissolution of iron in acidic media. Research findings in recent times have focused on emerging cheap, non-toxic drugs as environment responsive corrosion inhibitors [17-24].

Literature review indicates that few antibiotics have been reported as corrosion inhibitors for steel and aluminum corrosion in acidic and alkaline media [25]. Very recently, Hari Kumar et al. [26] used ampicillin drug as an inhibitor for mild steel corrosion in 1 M HCl. Nevertheless, as no concrete results have been published for the corrosion inhibition of zinc steel sheet in 5% NaCl with the use of sulfisoxazole (SSZ) as inhibitor, the present study has researched this method.

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The inhibition efficiencies of the compound were calculated using mass loss and electrochemical techniques. Rarely, the usage of hydrogen permeation measurement studies for this green inhibitor established the prominent performance of the inhibitors. This inhibitor is strong enough, amply planar and is able to block more galvanized steel surface areas.

Materials and methods

Materials

Zinc sheet specimens of size 1×4 cm² were used for mass loss and electrochemical studies. The aggressive solution of 3.5% NaCl [AR grade] was used for all the studies. The antibiotic namely sulfisoxazole was procured from Sigma Aldrich. The structure of the green inhibitor is given in Fig. 1, which also includes 13 C-NMR shifts. Electrochemical experiments were performed with a three electrode cell assembly with zinc samples as working electrode, platinum as counter electrode and saturated calomel [SCE] as reference electrode.

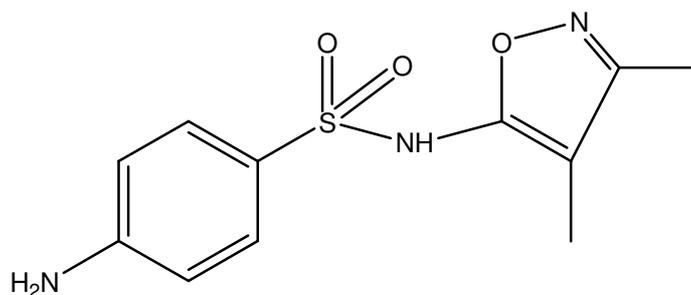


Figure 1. Structure of sulfisoxazole.

Mass loss studies

Mass loss and hydrogen permeation studies were done as described earlier [27]. The inhibitor concentrations used for weight loss and electrochemical studies were from 10 ppm to 100 ppm. Zinc metal specimens of size 1×4 cm² were abraded with different emery papers, and then degreased with acetone. The cleaned surfaces were washed with double distilled water, air dried and preserved in the desiccator. The mass loss study was followed at room temperature for three hours in 5% NaCl. The inhibition efficiency (IE%) according to mass loss was calculated by the following equation:

$$\text{Inhibition efficiency (IE\%)} = (W_a - W_p / W_a) \times 100 \quad (1)$$

where W_a and W_p are the weight loss values in the absence and presence of the green inhibitor.

Potential-current measurements by electrochemical studies

Potentiodynamic polarization measurements were monitored in a conventional three electrode cylindrical glass cell, using CH electrochemical analyser at a scan rate of 5 mV s⁻¹. Before carrying out the polarization measurements, the solution

was deaerated for 20 min, and the working electrode was maintained at its corrosion potential for 20 min, until a steady state was obtained. The zinc surface was immersed into various inhibitors concentrations in 100 mL of 5% NaCl, at room temperature. The inhibition efficiency (IE%) was calculated using the following equation:

$$\text{Inhibition efficiency (IE\%)} = (I_a - I_p / I_a) \times 100 \quad (2)$$

where I_a and I_p are the corrosion current densities without and with the green inhibitor, respectively.

The potentiodynamic current-potential curves were recorded by automatically changing the electrode potential from -950 mV to +100 mV versus the open circuit potential. The corresponding corrosion current (I_{corr}) was recorded. Tafel plots were made by plotting E versus log I. Corrosion potential (E_{corr}), corrosion current density (I_{corr}) and cathodic and anodic slopes (β_c and β_a) were calculated according to known procedures.

Impedance measurements were done in the frequency range from 0.1 to 10000 Hz, by means of amplitude of 20 mV and 10 mV peak to peak, with an AC signal at open-circuit potential. Charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) values were obtained from the Nyquist plot [28-30]. The percentage inhibition efficiency was calculated from the following equation:

$$\text{Inhibition efficiency (IE\%)} = (C_{\text{dl}}^{\text{a}} - C_{\text{dl}}^{\text{p}} / C_{\text{dl}}^{\text{a}}) \times 100 \quad (3)$$

where C_{dl}^{a} and C_{dl}^{p} are the charge transfer resistance of zinc sheets, without and with green inhibitor, respectively.

Results and discussion

Mass loss studies

The values of inhibition efficiency (IE%) and surface coverage (θ) calculated for the green inhibitor at different concentrations, for the corrosion reaction of zinc sheets in 3.5% NaCl from the mass loss data, are summarized in Table 1. It was established that the inhibition efficiency increased with higher inhibitor concentrations. It was also ostensible that the corrosion rate decreased higher with green inhibitor concentrations. It was clear that the inhibitors retarded the zinc sheet corrosion at all the concentrations used in the study. Maximum inhibition efficiency was observed at 100 ppm concentrations of sulfisoxazole.

Potential-current measurements by electrochemical studies

Polarization results, such as the values of corrosion potential (E_{corr}), corrosion current densities (I_{corr}), anodic Tafel slope (β_a), cathodic Tafel slope (β_c), surface coverage (θ) and inhibition efficiency (IE%), were calculated using polarization curves for the corrosion of zinc sheets in 3.5% NaCl, and are summarized in Table 2. It can also be seen from the table that the corrosion current (I_{corr}) value

declines with an increase in the green inhibitor concentration. Further, it was established that increasing concentrations of sulfisoxazole enhanced the values of both β_a and β_c , in a random manner.

Hence, corrosion inhibition by this compound was under cathodic control, but chiefly under mixed type. The inhibition efficiency (IE%) and surface coverage (θ) increased with higher SSZ dosages in the experiment. The maximum inhibition efficiency was obtainable at a concentration of 100 ppm. A definite relationship exists between the results obtained from mass loss and potential-current studies for the above inhibitor.

Table 1. Values of inhibition efficiency and surface coverage for the dissolution of zinc in 3.5% NaCl, in the presence of different concentrations of sulfisoxazole, obtained from mass loss measurements.

Inhibitor concentrations (ppm)	Inhibitor efficiency (IE) (%)	Surface coverage (θ)
Sulfisoxazole		
Blank	-	-
30 ppm	75.42	0.75
70 ppm	87.87	0.88
100 ppm	98.32	0.98

Table 2. Electro kinetic parameters and inhibition efficiency for zinc corrosion in 3.5% NaCl, obtained by the polarization method in sulfisoxazole presence.

Inhib. conc. (ppm)	E_{corr} (mV vs. SCE)	I_{corr} ($\mu\text{A cm}^{-2}$)	β_a (mV dec ⁻¹)	β_c (mV dec ⁻¹)	IE (%)	θ
Blank	-856.68	645.15	100.2	150.5	-	-
Sulfisoxazole						
30	-832.25	159.79	81.5	128.2	75.01	0.75
70	-800.52	76.87	97.4	134.4	87.97	0.88
100	-791.69	10.43	74.2	101.2	98.34	0.98

Electrochemical impedance studies

The Nyquist representations of zinc's impedance behaviour in 3.5% NaCl, with and without the addition of various inhibitors concentrations, are given in Table 3.

Table 3. Electrochemical impedance parameters for the dissolution of the zinc sheet rod in 5% NaCl, with and without the SSZ compound.

Inhibitor conc. (ppm)	R_{ct} ($\Omega \text{ cm}^2$)	C_{dl} (F cm ⁻²)	IE (%)	Surface coverage (θ)
Blank	47.2	0.296	-	-
Sulfisoxazole				
30	127.35	0.0734	75.07	0.75
70	189.42	0.0381	86.78	0.87
100	280.73	0.0048	98.35	0.98

The table also contains the values of charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) derived from Nyquist plots, for the dissolution of zinc in

sea water. R_{ct} values were seen to increase with higher concentrations of the green compound in sea water.

It was found that C_{dl} values were brought down by enhancing sulfisoxazole concentrations in the sea water medium. This can be accredited to the increasing adsorption of the inhibitor onto the metal surface with higher concentrations [33].

Adsorption isotherm

The degree of surface coverage (θ) for different sulfisoxazole concentrations in 5% NaCl has been calculated from weight loss, polarization and electrochemical impedance studies. The obtained data were graphically tested for fitting the suitable isotherm [34-36]. A straight line was observed by plotting $\log(C/\theta)$ vs. $\log C$, which ratifies that the adsorption of this green inhibitor observed Langmuir adsorption isotherm.

The Langmuir isotherm for the adsorbed layers is given by the following equation [37]:

$$C_{inh}/\theta = 1/K_{ads} + C_{inh} \quad (4)$$

where K_{ads} is the equilibrium constant of the adsorption/desorption process. The adsorption equilibrium constant (K_{ads}) and free energy of adsorption [ΔG°_{ads}] were calculated using the following equations [38]:

$$K_{ads} = 1/C_{inh} \times \theta / 1-\theta \quad (5)$$

$$\Delta G^{\circ}_{ads} = -2.303RT \log [55.5K_{ads}] \quad (6)$$

where 55.5 is the molar concentration of water in the solution [38-39], R is the gas constant and T is the temperature. The values of the adsorption equilibrium constant (K_{ads}) and free energy of adsorption (ΔG°_{ads}) are given in Table 4. The negative values of ΔG°_{ads} showed that the adsorption of sulfisoxazole onto the zinc surface in a chloride environment was a spontaneous process. It is well-known that ΔG°_{ads} values of 20 kJmol⁻¹ or lower indicate physisorption, while those of -40 kJmol⁻¹ or higher involve charge sharing or transfer from the inhibitors to the metal surface, to form a co-ordinate bond, of which process is known as chemisorption. The values of the free energy of adsorption (ΔG°_{ads}) in this study ranged from -28 to -32 kJmol⁻¹, demonstrating that the adsorption was not just a physisorption process, as it may include some other interactions [40-43].

Table 4. Gibbs free energy parameters and adsorption equilibrium constant (K_{ads}) of the green inhibitor (SSZ), at different temperatures, evaluated by mass loss method.

Temperature [K]	K_{ads} Green inhibitor	$-\Delta G^{\circ}_{ads}$ [kJmol ⁻¹]
313	931	28.33
323	1164	29.82
333	1341	31.17

Mechanism of inhibition

In sulfisoxazole, the presence of lone pairs of electrons of nitrogen and sulfur atoms of both benzamino and sulfoxide groups, along with an oxygen atom, favours the adsorption of sulfisoxazole onto oxidized zinc surfaces, by virtue of donating electrons to the positively charged Fe atoms, when exposed to a chloride environment.

Quantum mechanical studies

Quantum mechanical calculations were carried out to explore the adsorption and inhibition mechanisms of the SSZ compound on the corrosion of galvanized steel surfaces in 5% NaCl. Figs. 2 and 3 indicate HOMO and LUMO structure of sulfisoxazole. The values of calculated quantum chemical parameters, i.e., E_{HOMO} (highest occupied molecular orbital), E_{LUMO} (lowest unoccupied molecular orbital), ΔE (energy gap), μ (dipole moment), etc., are presented in Table 5. E_{HOMO} is related to the electron-releasing capability of the inhibitor molecule, while E_{LUMO} is associated to electrons with the drawing capacity of the inhibitor molecule. In the present investigation, donor-acceptor interactions between the π -electrons of nitrogen and sulphur atoms of benzamino and sulfoxide groups favoured the effective adsorption of SSZ onto zinc surfaces, which is evidenced from the dense electrons clouds in HOMO and LUMO structure, which are similar in both orbitals. It is well understood that if both HOMO and LUMO structures resemble each other, the resultant inhibitor adsorption will be better onto the metal surface. The gap between HOMO–LUMO energy levels of molecules was another important factor that needed to be considered. The higher is ΔE value of an inhibitor, the higher is its inhibition efficiency. It has been reported that large values of the dipole moment will improve corrosion inhibition. Based on the values of ΔE and dipole moment, the SSZ compound has been strongly adsorbed onto the galvanized steel surface immersed in 5% NaCl.

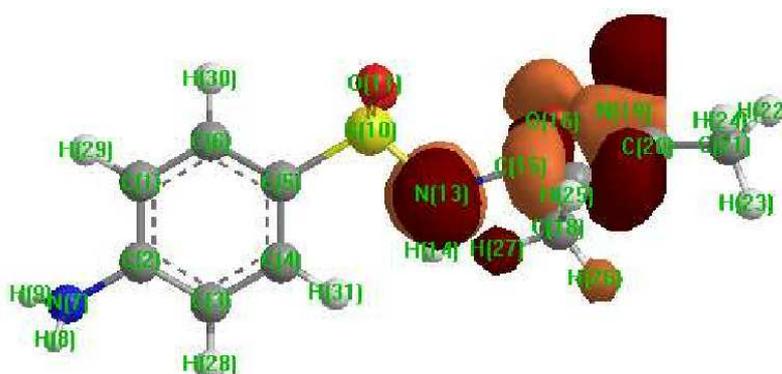
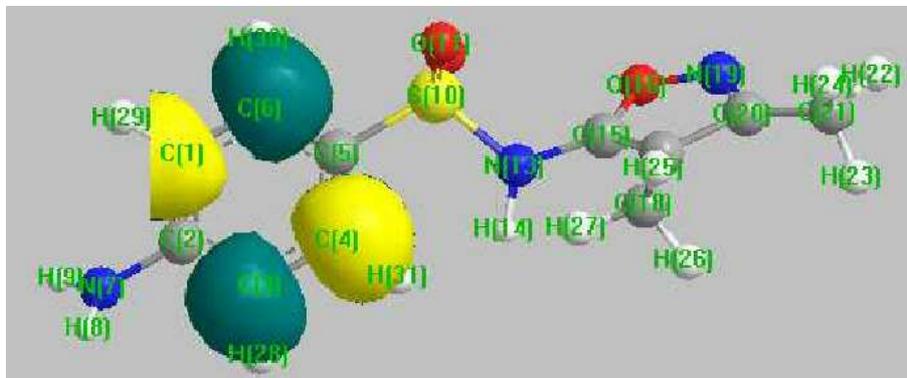


Figure 2. Highest molecular orbital of SSZ molecules during its adsorption onto zinc surfaces.

Table 5. Quantum mechanical parameters for sulfisoxazole for the corrosion of zinc surfaces.

Inhibitor	LUMO (eV)	HOMO (eV)	ΔE (cal.mol ⁻¹)	Dipole moment (Debye)
Sulfisoxazole (SSZ)	-0.6023	-8.1775	7.5752	3.8

**Figure 3.** Lowest unoccupied molecular orbital of SSZ molecules during its adsorption onto zinc surfaces.

Conclusion

The controlled dissolution of zinc surfaces was monitored in 3.5% NaCl solutions at different temperatures (313–333 K), without and with various concentrations of sulfisoxazole, a green inhibitor, by adapting chemical and electrochemical methods. The main conclusions are:

1. Sulfisoxazole effectively exhibited inhibiting properties for galvanized steel corrosion in 3.5% NaCl;
2. Tafel polarization plots designated that the present inhibitor showed a mixed mode of inhibition;
3. the rates of corrosion obtained from the impedance measurements were in good agreement with those recorded using potentiodynamic polarization. This confirms the validity of the corrosion rates measured by the potentiodynamic polarization;
4. the adsorption of sulfisoxazole on zinc surfaces obeyed Langmuir isotherm;
5. apparent activation energies in the presence of sulfisoxazole for the corrosion of zinc in chloride media ranged from 28 to -32 kJmol⁻¹, demonstrating that the adsorption was not just physisorption;
6. quantum mechanical results confirmed the remarkable performance of SSZ inhibitor through its real adsorption onto zinc surfaces exposed to 3.5% NaCl.

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