



CORROSION INHIBITION BY TRYPTOPHAN- Zn^{2+} SYSTEM FOR CARBON STEEL IN SEA WATER

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The inhibitive effect of Tryptophan- Zn^{2+} system in controlling the corrosion of carbon steel in sea water was investigated by weight loss method. Results of weight loss method indicated inhibition efficiency increased with increasing the inhibitor concentration. The corrosion inhibition was observed due to the formation of more stable and compact protective film on the metal surface. The surface morphology of the protective film on the metal surface was analyzed by FTIR and AFM analysis.

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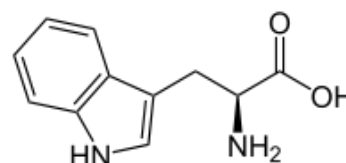
INTRODUCTION

The corrosion process in deep seawaters occurs under very specific conditions and is characterized mainly by low temperature, high chloride contents, low oxygen content, the presence of CO_2 and H_2S , microorganisms and high contents of dissolved salts.¹⁻⁴ Seawater systems are used by many industries such as shipping, offshore oil and gas production, power plants and coastal industrial plants. The main use of seawater is for cooling purposes but it is also used for fire fighting, oil field water injection and for desalination plants.

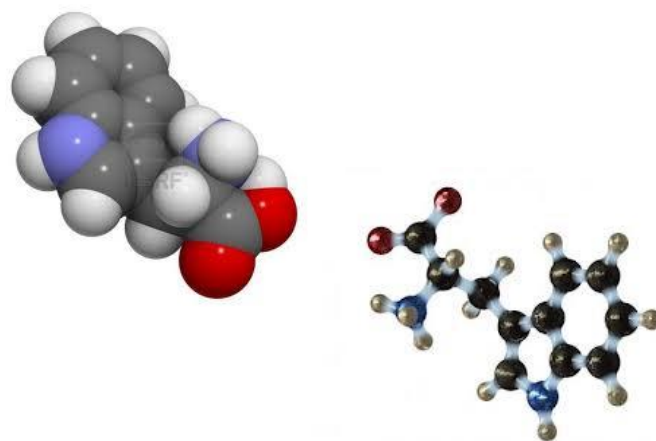
Tryptophan is a non-toxic, relatively cheap amino acid that is easy to produce in purity greater than 99%. Amino acids are nontoxic, relatively cheap, and easy to produce with purities greater than 99%. Recently, with respect to amino acid as corrosion inhibitor, many achievements have been gained in laboratory studies.⁵⁻¹⁰ Furthermore, as environmental and non-phosphorus corrosion and scale inhibitors, poly (aspartic acid) and poly (epoxy succinic acid), which are the amino acid derivatives, have been widely used in industrial recirculating cooling water systems, showing an excellent performances.^{11, 12}

Tryptophan is a derivative of indole ring. Based on the analysis of molecule structure of tryptophan Figure 1, it has the potential to become an excellent corrosion inhibitor. Ashassi-Sorkhabi et al.¹³ reported that compared with the other amino acids, including alanine, leucine, valine, proline, and methionine, tryptophan exhibited the best inhibition efficiency toward the corrosion of aluminum in 1 M HCl + 1 M H_2SO_4 , which was attributed to the excess nitrogen atoms in molecule structure and the relatively large molecule volume.

Molecular structure of tryptophan is shown in scheme 1. Space filling model of tryptophan is shown in scheme 2.



Scheme 1. Tryptophan or (2S)-2-amino-3-(1H-indol-3-yl)propanoic acid



Scheme 2. Space filling model of tryptophan

The present work is under taken to evaluate the inhibition efficiency of tryptophan- Zn^{2+} system in controlling corrosion of carbon steel immersed in the absence and presence of Zn^{2+} by weight loss method and to analyse the protective film by FTIR and AFM method.

MATERIALS AND METHODS

Preparation of specimen

Carbon steel specimens [0.0267 % S, 0.06 % P, 0.4 % Mn, 0.1 % C and the rest iron] of dimensions 1.0 cm x 4.0 cm x 0.2 cm were polished to a mirror finish and degreased with trichloroethylene.

Weight-loss method

Carbon steel specimens in triplicate were immersed in 100 mL of the sea water (Table 1) containing various concentrations of the inhibitor in the presence and absence of Zn²⁺ for one day. The weight of the specimens before and after immersion was determined using a Shimadzu balance, model AY62. The corrosion products were cleansed with Clarke's solution.¹⁴ The inhibition efficiency (*IE*) was then

$$IE = 100 \left(1 - \frac{W_2}{W_1} \right) \quad (1)$$

calculated using the equation:

where

- W_1 corrosion rate in the absence of the inhibitor,
- W_2 corrosion rate in the presence of the inhibitor.

Corrosion rate (*CR*, in mm year⁻¹) was calculated using the formula.

$$CR = 87.6 \frac{W}{DAT} \quad (2)$$

where

- W weight loss in milligram
- D density of specimen g cm⁻³
- A area of specimen in square cm
- T exposure time in hours

Surface examination study

The carbon steel specimens were immersed in various test solutions for a period of 1 day. After 1 day, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimen was analyzed by surface analysis techniques.

FTIR spectra

The film formed on the metal surface was carefully removed and mixed thoroughly with KBr. The FTIR spectra were recorded in a perkin elmer 1600 spectrophotometer.

Atomic Force Microscopy characterization (AFM)

The carbon steel specimen 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 microscopy (Veeco Dinnova 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 s⁻¹.

RESULTS AND DISCUSSION

Analysis of Weight loss Study

The corrosion inhibition efficiencies of tryptophan-Zn²⁺ systems are given in the Table 2.

Table 1. Physicochemical parameters of sea water (Ramnad, Tamil Nadu, India)

Parameters	Results
Total dissolved solid mg L ⁻¹	50787 ppm
Electrical conductivity	74687 μS cm ⁻¹
pH	8.14
Total hardness as CaCO ₃	11500 ppm
Calcium	1400 ppm
Magnesium	1920 ppm
Chloride	25750 ppm
Sulphate	1033 ppm

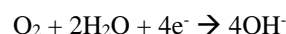
The calculated corrosion inhibition efficiency (*IE*) and corrosion rate (*CR*) of tryptophan in controlling corrosion of carbon steel in sea water, for a period of one day in absence and presence of zinc ion are given in Table 2.

It is observed from the Table 2 the calculated value indicates the ability of Tryp to be a good inhibitor. The *IE* is found to be enhanced in the presence of Zn²⁺ ion. tryp alone shows some inhibition efficiency. For example 250 ppm of tryptophan shows 48% of *IE*. The concentration of tryptophan increases, the *IE* also increases. Similarly for a given concentration of tryptophan, the *IE* increases as the concentration of Zn²⁺ increases. A synergistic effect exists between tryp and Zn²⁺. For example, 20 ppm of Zn²⁺ has 41 percent of *IE*; 250 ppm of tryptophan has 48 percent *IE*. Interestingly their combination has High *IE*, namely, 79 %.¹⁵⁻¹⁷

Therefore the mixture of inhibitors shows better *IE* than individual inhibitors. In the presence of Zn²⁺, more amount of tryp is transported towards the metal surface. Fe²⁺-tryp complex is formed on the anodic sites of the metal surface. Thus the anodic reaction is



controlled. The cathodic reaction is the generation of OH⁻



which is controlled by the formation of Zn(OH)₂ on the cathodic sites of the metal surface. Thus the anodic reaction and cathodic reaction are controlled effectively. This accounts for the synergistic effect existing between Zn²⁺ and tryptophan.^{18, 19}

Synergism parameter

Synergism parameters (S_I) have been used to known the synergistic effect existing between two inhibitors. S_I value is found to be greater than one suggesting that the existence of synergistic effect between the inhibitors.^{20, 21}

In Table 3 synergism parameters were calculated using the relation

$$S_I = \frac{1 - \theta_{1+2}}{1 - \theta_1 - \theta_2} \quad (3)$$

where

θ_{1+2} is equal with $(\theta_1 + \theta_2) - (\theta_1 \theta_2)$

θ_1 is the surface coverage of inhibitor (tryp)

θ_2 is the surface coverage of inhibitor (Zn²⁺)

θ'_{1+2} is the combined surface coverage of inhibitors (tryptophan) and (Zn²⁺)

The surface coverage is:

$$S = \frac{IE(\%)}{100} \quad (4)$$

From the Table 3 it can be seen that the values of S_I greater than unity, suggesting that the phenomenon of synergism existing between tryp- Zn²⁺.

Table 2. Inhibition efficiencies (IE) and corrosion rates (CR) obtained from tryp - Zn²⁺ systems, when the carbon steel immersed in sea water. Inhibitor system: - tryptophan- Zn²⁺

Tryptophan (ppm)	Zn ²⁺ (0 ppm)		Zn ²⁺ (20 ppm)	
	IE %	CR mm y ⁻¹	IE%	CR, mm y ⁻¹
0	-	0.1809	41	0.1067
50	2	0.1773	43	0.1031
100	10	0.1628	53	0.0796
150	26	0.1339	66	0.0615
200	28	0.1302	66	0.0615
250	48	0.0941	79	0.0379

Table 3. Synergism parameter (S_I) for carbon steel immersed in Sea water in the absence and presence of inhibitors.

Tryp (ppm)	θ_1	θ_2 (Zn ²⁺ - 20 ppm)	θ'_{1+2}	S_I
50	0.02	0.41	0.43	1.0143
100	0.10	0.41	0.43	0.9315
150	0.26	0.41	0.66	1.6029
200	0.28	0.41	0.66	1.2471
250	0.48	0.41	0.79	1.4609

Analysis of FTIR Spectra

FTIR spectrometer is a power instrument that is used to determine the formation of bonds for organic inhibitors adsorbed on the metal surface. FTIR spectra have been used to analyze the protective film formed on metal surface. The structure of tryptophan is shown in scheme 1. The space filling model of tryptophan is shown in scheme 2. FTIR

spectrum of pure tryp is given in (Figure 1.) The CN stretching frequency appears at 1237 cm⁻¹. The C=O stretching frequency of carboxyl group appears at 1661 cm⁻¹. The NH stretching frequency appears at 3402 cm⁻¹. The aromatic ring appears at 1410 cm⁻¹.

The FTIR spectrum of the film formed on the metal surface after immersion in the sea water for 1 day containing 250 ppm of tryp and 20 ppm of Zn²⁺ is shown in (Fig 2.) The CN stretching frequency has shifted from 1237 to 1229 cm⁻¹. The C=O stretching frequency shifted from 1661 to 1637 cm⁻¹. The NH stretching frequency shifted from 3402 to 3429 cm⁻¹. This indicates that the nitrogen atom of Tryp has coordinated with Fe²⁺ formed on the metal surface resulting in the formation of Fe²⁺- Tryp complex on the anodic sites of the metal surface. The peak at 1366 cm⁻¹ is due to Zn-O stretching. The stretching frequency due to -OH appears at 3033 cm⁻¹. Thus FITR study leads to the conclusion that the protective film consist of Fe²⁺-tryp complex and Zn (OH)₂ on the metal surface.^{22- 26}

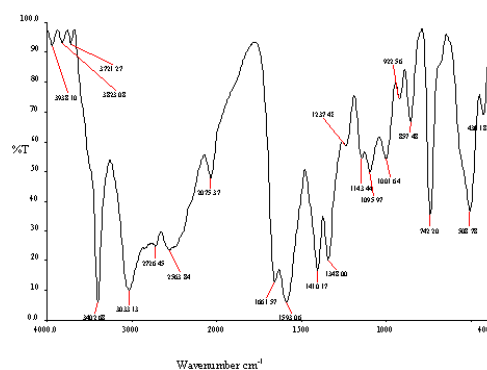


Figure 1. FTIR spectrum of pure tryptophan

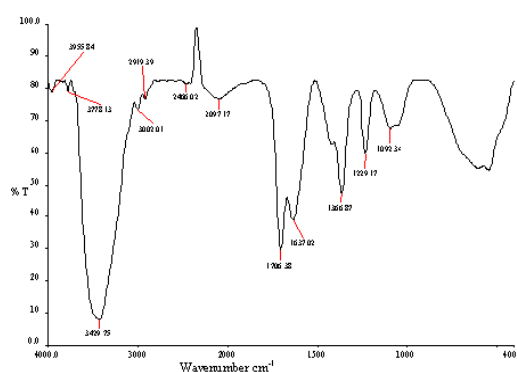


Figure 2. Film formed on metal surface after immersion in the solution containing sea water + tryptophan (250 ppm) + Zn²⁺ (20 ppm)

Atomic Force Microscopy Characterization

Atomic force microscopy (AFM) or scanning force microscopy (SFM) is a very high-resolution type of scanning probe microscopy, with demonstrated resolution

on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit.

due to atmospheric corrosion. Fig. 3b and 3e displays the corroded metal surface with few pits in the absence of the

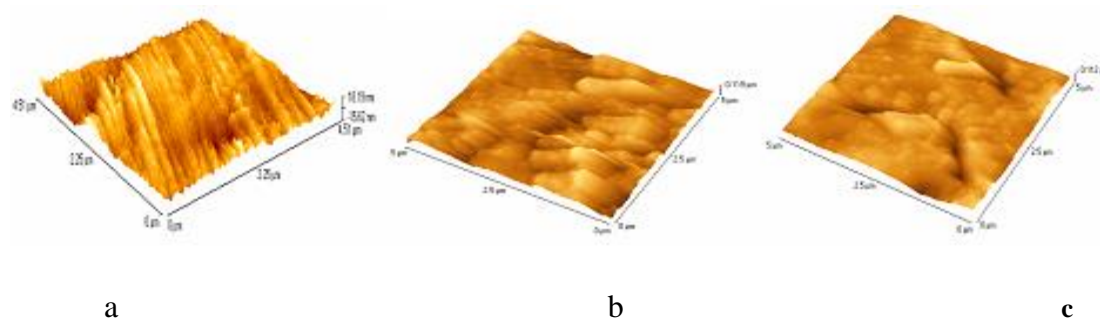


Figure 3. Three dimensional AFM images of the surface of: a) As polished carbon steel (control); b) carbon steel immersed in sea water (blank); c) carbon steel immersed in sea water containing tryp (250 ppm) + Zn²⁺ (20 ppm)

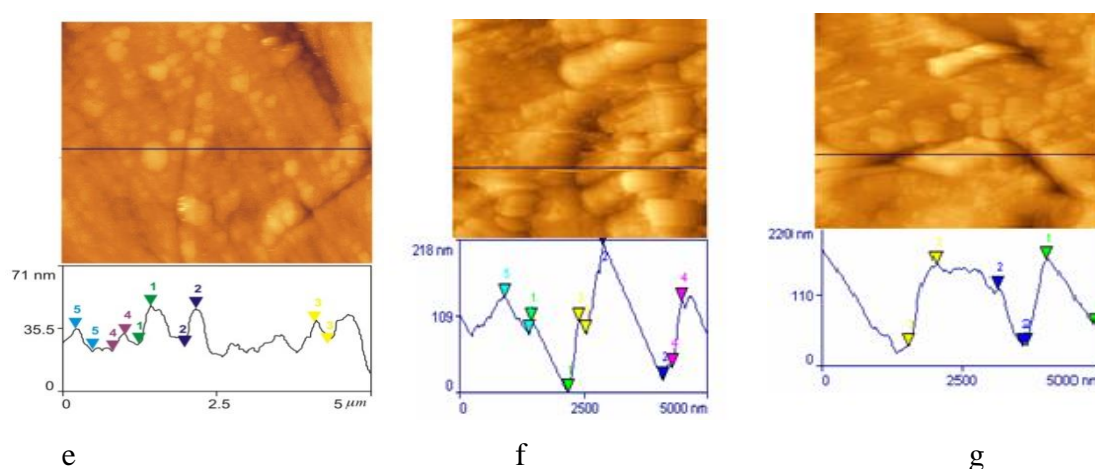


Figure 3. AFM cross-sectional images of the surface of: d) As polished carbon steel (control); e) carbon steel immersed in sea water (blank); f) carbon steel immersed in sea water containing tryp (250 ppm) + Zn²⁺ (20 ppm).

The three dimensional (3D) AFM morphologies and the AFM cross-sectional profile for polished carbon steel surface (reference sample), carbon steel surface immersed in sea water (blank sample) and carbon steel surface immersed in sea water containing the formulation of 250 ppm of tryptophan and 20 ppm of Zn²⁺ are shown as Fig. 3a and 3d, Fig. 3b and 3e and Fig. 3c and 3f respectively.

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). Table 4 is a summary of R_q , R_a , and $P-V$ value for carbon steel surface immersed in different environment.

Fig. 3a and 3d displays the surface topography of uncorroded metal surface. The value of R_q , R_a and $P-V$ height for the polished carbon steel surface (reference sample) are 4.3 nm, 3.41 nm and 35.28 nm respectively. The slight roughness observed on the polished carbon steel surface is

inhibitor immersed in sea water. The R_q , R_a and $P-V$ height values for the carbon steel surface are 40.2 nm, 31.0 nm and 191.9 nm respectively. These data suggests that carbon steel surface immersed in sea water has a greater surface roughness than the polished metal surface, which shows that the unprotected carbon steel surface is rougher and was due to the corrosion of the carbon steel in sea water environment.

Fig. 3c and 3f displays the steel surface after immersion in sea water containing 250 ppm of tryp and 20 ppm of Zn²⁺. The R_q , R_a and $P-V$ height values for the carbon steel surface are 25.8 nm, 19.7 nm and 71.53 nm respectively. The R_q , R_a and $P-V$ 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⁺-tryptophan complex and Zn(OH)₂ on the metal surface thereby inhibiting the corrosion of carbon steel.²⁷⁻³⁰

Mechanism of Corrosion inhibition

The results of the weight-loss study show that the formulation consisting of 250 ppm of tryptophan and 20 ppm of Zn²⁺ has 79% IE in controlling corrosion of carbon steel in sea water. A synergistic effect exists between Zn²⁺

and Tryp. FTIR spectra reveal that the protective film consists of Fe²⁺-Tryp complex and Zn(OH)₂. In order to explain these facts the following mechanism of corrosion inhibition is proposed.

Table 4. AFM data for carbon steel surface immersed in inhibited and uninhibited environment.

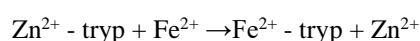
Sample	RMS Roughness R _q , nm	Average Roughness, R _a , nm	Max. Peak-to-valley height, nm
Polished carbon steel	4.33	3.41	35.28
Carbon steel immersed in sea water (blank)	40.2	31.0	191.9
Carbon steel immersed in 250 ppm of tryp-20 ppm Zn ²⁺	35.5	27.7	103.9

When the solution containing sea water, 20 ppm Zn²⁺ and 250 ppm of tryp is prepared, there is formation of Zn²⁺-Tryp complex in solution.

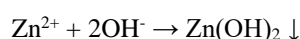
When carbon steel is immersed in this solution, the Zn²⁺-Tryp complex diffuses from the bulk of the solution towards metal surface.

Zn²⁺- tryp complex diffuses from the bulk solution to the surface of the metal and is converted into a Fe²⁺-Tryp complex, which is more stable than Zn²⁺- tryp.

On the metal surface Zn²⁺-Tryp complex is converted in to Fe²⁺-Tryp on the anodic sites. Zn²⁺ is released



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



Thus the protective film consists of Fe²⁺-Tryp complex and Zn (OH)₂. The FTIR and AFM images confirm the formation of protective layer on the metal surface.

CONCLUSIONS

The present study leads to the following conclusions.

The formulation consisting of 250 ppm tryp and 20 ppm Zn²⁺ has 79% inhibition efficiency to carbon steel immersed in sea water.

FTIR spectra reveal that the protective film consists of tryp- Fe²⁺ complex.

The AFM analysis reveals that the protective film is formed on the metal surface.

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