Corrosion Inhibition of Mild Steel in Sulphuric acid medium by Thio Urea – Zn^{2+} system

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Abstract

The inhibition efficiency (IE) of Thiourea in controlling corrosion of Mild steel in sulphuric acid media at pH-4 in the absence and presence of Zn^{2+} has been evaluated by weight loss method. The formulation consisting of 250 ppm of Thiourea and 25 ppm Zn^{2+} has 82% IE. It is found that the inhibition efficiency (IE) of Thiourea increases by the addition of Zn^{2+}ion. A synergistic effect exists between Thiourea and Zn^{2+}. Polarization study reveals that Thiourea – Zn^{2+} system controls the cathodic reaction predominantly and suggests the formation of protective film on the metal surface. The nature of the protective film formed on the metal surface has been analyzed by FTIR spectra and SEM. The protective film is found to consist of Fe^{2+} – Thiourea complex and $Zn(OH)_2$. Based on the above studies a suitable mechanism has been proposed for the corrosion inhibition.

1. Introduction

Corrosion is the deterioration of metals and alloys by electrochemical reaction with its environment. It is a natural phenomenon which cannot be avoided, but it can be controlled and prevented using the suitable preventive measures like metallic coating, anodic protection, cathodic protection and using inhibitors. Inhibitors are playing very good role in the process of corrosion control. The organic compounds containing hetero atoms such as oxygen, nitrogen, phosphorus and sulphur, etc have been employed as corrosion inhibitors to protect the metals from corrosion[1-4]. The corrosion inhibition of thiourea (TU) and its derivatives have been extensively investigated in various aqueous corrosive media[5-7]. As TU molecule (Fig.1) contains one sulphur and two nitrogen atoms; hence thiourea and its derivatives can function as very good corrosion inhibitors[8-9].

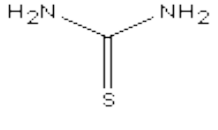


Fig 1 Structure of Thiourea

The present work is to evaluate the inhibition efficiency of TU- Zn^{2+} system in controlling corrosion of Mild steel immersed in sulphuric acid media at pH-4 in the absence and presence of Zn^{2+} by weight loss method and to analyze the protective film by FTIR and SEM.

2. EXPERIMENTAL

2.1Preparation of the specimens:

Mild steel specimen (0.026% S, 0.06% P, 0.4% Mn and 0.1% C and rest iron) of the dimensions 1.0 X 4.0 X 0.2 cm were polished to a mirror finish and degreased with trichloroethylene and used for the weight-loss method and surface examination studies.

2.2Weight – Loss Method:

Mild steel specimens in duplicate were immersed in 100 ml of the Sulphuric acid medium at pH-4 containing various concentrations of inhibitor in the presence and absence of Zn^{2+} for one day. The corrosion product cleaned with Clark's solution[10]. The weights of the specimens before and after immersion were determined using a balance, Shimadzu AY62 model.

Then the Inhibition Efficiency was calculated using the equation (1)

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

Where W_1 and W_2 are Corrosion rate in the absence and presence of inhibitor respectively.

The corrosion rate (CR) was calculated using the formula

87.6 W/DAT mmpy

Where,

W = weight loss in mg, D = 7.87 g/cm^3,

A = surface are of the specimen (10 cm^2), T = 24 hrs.

3. Potentiodynamic Polarization Study:

Polarization study was carried out in Electrochemical Impedance Analyzer model CHI 660A using a three electrode cell assembly. The working electrode was used as a rectangular specimen of Mild steel with one face of the electrode of constant 1 cm^2 area exposed. A saturated calomel electrode (SCE) was used as reference electrode. A rectangular platinum foil was used as the counter electrodes. Polarization curves were recorded after doing iR compensation. The corrosion parameters such as Tafel slopes (anodic slope b_a and cathodic slope b_c), corrosion current (ICorr) and corrosion potential (ECorr) values were calculated. During the polarization study, the scan rate (V/s) was 0.005; Hold time at Ef (s) was zero and quiet time (s) was 2.

4. Surface Examination Study:

The Mild steel specimens immersed in various test solutions for one day were taken out and dried. The nature of the film formed on the protective film formed on the surface of the metal specimen was analyzed by various surface analysis techniques.

4.1FTIR spectra:

The Mild steel specimens immersed in various test solutions for one day were taken out and dried. The film formed on the metal surface was carefully removed and thoroughly mixed with KBr, so as to make it uniform throughout. The FTIR spectra were recorded in a Perkin –Elmer– 1600 spectrophotometer.

4.2 Scanning Electron Microscopy (SEM)

The Mild steel immersed in blank solution and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water, dried and observed in a scanning electron microscope to examine the surface morphology. The surface morphology measurements of Mild steel were examined using JEOLMODEL6390 computer controlled scanning electron microscope.

5. RESULTS AND DISCUSSION

5.1Analysis of results of weight loss study:

The calculated Inhibition efficiencies (IE) and corrosion rates of TU in controlling corrosion of Mild steel immersed in sulphuric acid media at pH-4 in the absence and presence of Zn^{2+} ion are given in **Table 1.**

The calculated value indicates the ability of TU to be a good corrosion inhibitor. The IE is found to be enhanced in the presence of Zn^{2+} ion. TU alone shows 55 % IE. But the combination of 250 ppm TU and 25 ppm Zn^{2+} shows 82% IE. This suggests a synergistic effect exists between TU and Zn^{2+} [11- 15].

Table 1: Inhibition efficiencies (IE %) obtained from TU - Zn^{2+} systems, when Mild steel immersed in Sulphuric acid media at pH-4

Inhibitor system: TU + Zn^{2+}

Immersion period: 1 day

TU ppm	Zn^{2+} (0 ppm)		Zn^{2+} (25 ppm)	
	IE %	CR mmpy	IE %	CR Mmpy
0	0	0.01947	10	0.01947
50	38	0.1205	55	0.1762
100	45	0.1113	65	0.0881
150	48	0.1020	74	0.0672
200	50	0.0974	80	0.0510
250	55	0.0881	82	0.0394

5.2Analysis of Polarization curves:

The potentiodynamic polarization curves of Mild steel immersed in Sulphuric media at pH-4 in the absence and presence of inhibitors are shown in **Fig 2**

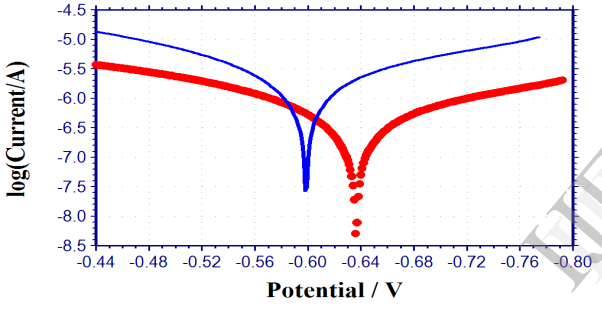


Fig 2 Polarization curves of Mild steel immersed in various test solutions

(a) Sulphuric acid media at pH-4

(b) Sulphuric acid media at pH-4 containing 250 ppm of Thiourea +25 ppm of Zn^{2+}

The corrosion parameters such as corrosion potential (ECorr), Tafel slopes (anodic slope ba and cathodic slope bc), linear polarization resistance and corrosion current (ICorr) values were calculated are given in **Table 2.**

When Mild steel is immersed in aqueous media at pH-4, the corrosion potential is – 598 mV Vs saturated calomel electrode (SCE). The corrosion current is $2.394x10^{-6}$ A/cm^2. When Thiourea (250 ppm) and Zn^2 (25 ppm) are added to the above system the corrosion potential is shifted to the cathodic side(from -598 mV to -638 mV). This suggests that the cathodic reaction is controlled predominantly. More over in presence of the inhibitor system, the corrosion current decreases from $2.394x10^{-6}$ A/cm^2 to $5.985x10^{-7}$ A/cm^2 and LPR value increases from 16724.9 ohm cm^2 to 36024.6 ohm cm^2 . These observations indicate the formation of protective film on the metal surface [16-19].

5.3Analysis of FTIR spectra:

The FTIR spectrum of pure TU is shown in **Fig.3 (a).** The C=S stretching frequency is appears at 1412.43 cm^{-1}. The N – H stretching and deformation frequencies appear at 3381.67 cm^{-1} and 1609.30 cm^{-1} respectively. The C – N stretching frequency appears at 1466.60 cm^{-1}.

The FTIR spectrum of the film formed on the metal surface after immersion in sulphuric acid media at pH-4 consisting TU (250 ppm) and Zn^{2+} (25 ppm) is shown in **Fig.3 (b).** The C=S stretching frequency has shifted from 1412.43 cm-1 to 1350.07 cm-1. The N – H stretching frequency has shifted from 3381.67 cm^{-1} to 3495.92 cm^{-1}. The N – H deformation frequency has shifted from 1609.30 cm^{-1} to 1578.41 cm^{-1}. The C – N stretching frequency has shifted from 1412.85 cm^{-1} to 1383.60 cm^{-1}. This indicates that the TU has coordinated with Fe^{2+} on the metal surface through sulphur atom of C=S group and nitrogen atom of N – H group resulting in the formation of Fe^{2+} - TU complex. The peak at 1424.85 cm^{-1} is due to Zn – O stretching. These observations indicate the presence of Zn $(OH)_2$ formed on the metal surface. Thus the FTIR study leads to the conclusion that the protective film consist of Fe2+ - TU complex and $Zn(OH)_2$ formed on the metal surface[20-22].

5.4Analysis of Scanning Electron Microscopy Images:

SEM provides a pictorial representation of the surface. To understand the nature of the surface film in the absence and presence of inhibitors and the extent of Corrosion of Mild steel, the SEM micrographs of the surface are examined. The SEM micrographs (X1000) of polished Mild Steel surface (control) in Fig. 4. (a) shows the smooth surface of the metal. This shows the absence of any corrosion products or inhibitor complex formed on the metal surface. The SEM micrographs (X 1000) of Mild steel specimen immersed in the sulphuric

Table 2: Corrosion Parameters of Mild steel sulphuric acid media in the absence and presence of inhibitors obtained by polarization method

TU	Zn^{2+} ppm	Ecorr mV vs SCE	bc mV/decade	ba mV/decade	LPR ohm cm^2	Icorr A/cm^2
0	0	-598	205	167	16724.9	$2.394x10^{-6}$
250	25	-638	209	178	66877.7	$5.985x10^{-7}$

acid media for one day at pH-4, in the absence and presence of inhibitor system are shown in Fig.4. (b) and Fig.4. (c) respectively. The SEM micrographs of Mild steel surface immersed in sulphuric acid media at pH-4 in Fig.4. (b) shows the roughness of the metal surface which indicates the corrosion of mild steel in sulphuric acid media. Fig.4. (c,) indicates that in the presence of 250 ppm TU and 25 ppm Zn^{2+} mixture in sulphuric media at pH-4, the surface coverage increases which in turn results in the formation of insoluble complex on the surface of the metal. In the presence of TU and $Zn^{2+,}$ the surface is covered by a thin layer of inhibitors which effectively control the dissolution of Mild steel [23-28]

5.3Mechanism of corrosion

With these discussions, a mechanism is proposed for the corrosion inhibition of Mild steel immersed in sulphuric acid at pH-4 by 250 ppm TU and 25 ppm Zn^{2+} system.

1. When the formulation consisting of 250 ppm of TU and 25 ppm of Zn^{2+} in sulphuric acid media at pH-4 marine media there is a formation of TU – Zn^{2+} complex in solution.

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

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

Zn^{2+} _TU + Fe^{2+} → Fe2+_ TU + Zn^{2+}

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

$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$

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

6. In acidic solution the anodic reaction is the formation of Fe^{2+}. This anodic reaction is controlled by the formation of TU – Fe^{2+} complex on the anodic site of the metal surface. The cathodic reaction is the generation of Hydrogen gas. It is controlled by the formation of $Zn(OH)_2$ on the cathodic sites of the metal surface.

Fe → Fe2+ + 2e- (Anode reaction)

$2H^+ + 2e^- \rightarrow H_2$ (Cathodic reaction)

Fe^{2+} + TU → Fe^{2+} -TU Complex

$Zn^{2+} + 2\ OH^- \rightarrow Zn(OH)_2$

7. This accounts for the synergistic effect of TU – Zn^{2+} system

6. Conclusions.

The present study leads to the following conclusions:

1. The inhibition efficiency (IE) of TU in controlling corrosion of Mild steel immersed in Sulphuric acid media at pH-4 in the absence and presence of Zn^{2+} has been evaluated by weight loss method.
2. The formulation consisting of 250 ppm TU and 25 ppm Zn^{2+} has 82% corrosion inhibition efficiency.
3. Polarization study reveals that TU – Zn^{2+} system controls the cathodic reaction predominantly.
4. FTIR spectra reveal that the protective film consists of Fe^{2+} – TU complex and $Zn(OH)_2$.
5. The SEM micrographs confirm the formation of protective layer on the metal surface.

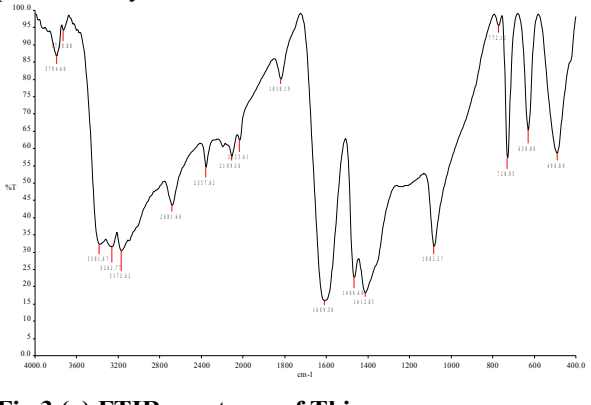


Fig 3 (a) FTIR spectrum of Thiourea

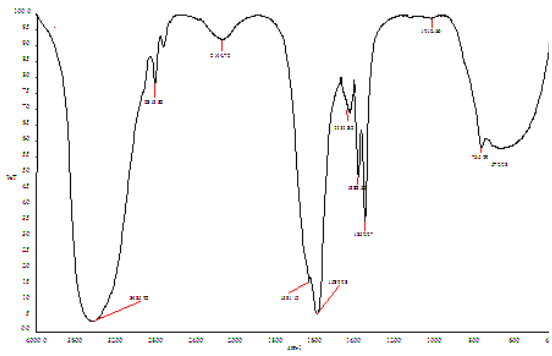
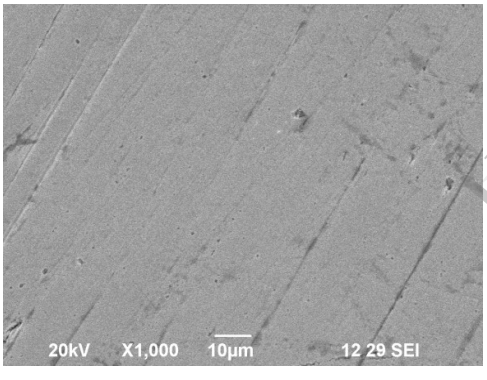


Fig 3 (b) The FTIR spectrum of the film formed on the metal surface after immersion in aqueous media at pH-4 consisting Thiourea (250 ppm) and Zn^{2+} 25 ppm)



Figure

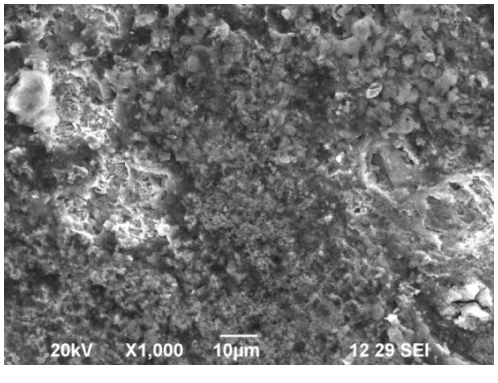
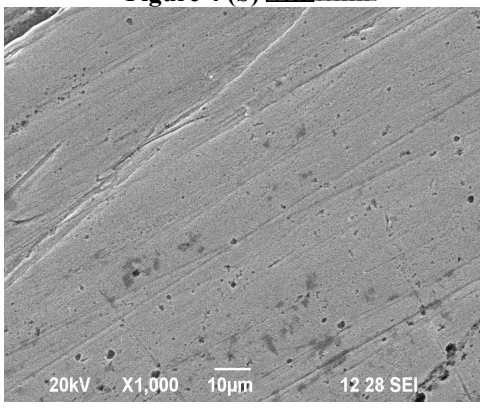


Figure 4 (b)



Figure

Fig .4(a) SEM micrographs of polished Mild steel Magnification – X 1000

4(b) Mild steel immersed in sulphuric acid media at pH-4 Magnification – X1000

4(c) Mild steel immersed in sulphuric acid media containing TU (250 ppm) + Zn^{2+} (25 ppm); .at pH-4 Magnification – X1000

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