Synergistic Effect of Thiourea-Zn^{2+} and L-Phenylalanine on the Inhibition of Corrosion of Mild Steel in Acid Medium

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Abstract—The formulation consisting of 100 ppm Thiourea, 25 ppm Zn^{2+} and 250 ppm of L-Phenylalanine has 95% corrosion inhibition efficiency with a synergistic effect among Thiourea, L-Phenylalanine and Zn^{2+} ions. Polarization study shows that this formulation as a mixed inhibitor. FTIR spectra exposed the presence of Fe^{2+}-Thiourea, Fe^{2+}-L-Phenylalanine complex and $Zn(OH)_2$ in protective film. AFM study confirmed the metal surface smoothness following engrossed in the inhibitor and the presence of formed protective film on the metal surface.

Keywords: *Corrosion, Mild Steel, Thiourea, Polarization, Atomic force Microscopy*

INTRODUCTION

Corrosion inhibition of Mild Steel (MS) is a matter of theoretical as well as practical importance. It has been widely used in industries such as pickling, cleaning, descaling, etc., and because of their aggressiveness, inhibitors are used to reduce the dissolution of metals. Many organic compounds containing N, S, O, & P have been reported as inhibitors (Bentiss *et al* .1999). Also the corrosion inhibition efficiency follows the order O < N < S < P. Among various organic compounds, Thiourea (TU) and its derivatives shows significant corrosion inhibition of metals and alloys in corrosive media. The corrosion inhibition of Thiourea and its derivatives have been extensively investigated in various aqueous corrosive media. As TU molecule contains one sulphur and two nitrogen atoms; hence Thiourea and its derivatives can function as very good corrosion inhibitors.

MATERIALS AND METHODS

Preparation of the Specimens

MS 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.

Elements	S	P	Mn	C	Fe
Composition	0.026	0.06	0.4	0.1	Rest

Preparation of Test Solutions

1 g of L-Phenylalanine was dissolved and made up to 100 ml in double distilled water in a standard flask. 1 ml of this solution was diluted to give 100 ml of 100 ppm of

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L-Phenylalanine. 1 g of Thiourea was dissolved in double distilled water and made up to 100 ml in a standard flask. 1 ml of this solution was diluted to give 100 ml of 100 ppm of TU. 25 ppm of Zinc Sulphate solution is also prepared.

Weight–Loss Method

MS specimens in duplicate were immersed in 100 ml of the sulphuric acid solution 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. The weights of the specimens before and after immersion were determined using a balance, Shimadzu AY62 model.

Then the Inhibition Efficiency was calculated using equation (1)

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

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

$$87.6\ W/DAT\ mm/y \quad (2)$$

Where W = weight loss in mg, D = 7.87 g/cm^3, A = surface area of the specimen (10 cm^2), T = 24 hrs

POLARIZATION STUDY

Polarization study was conducted in Electrochemical Impedance Analyzer model CHI 660A provided with iR compensation option. The system operates with three electrodes, one is the working, another is a counter electrode and the third is a reference electrode. The working electrode consists of a rectangular MS specimen with one electrode face of 1 cm^2 constant area exposed. The counter electrodes are a rectangular platinum foil. Saturated calomel electrode was used as the reference electrode. These three electrodes were immersed in the pH-4 H_2SO_4 solution in the absence and presence of inhibitor. The system was given a 5-10 min time gap to reach the steady state open circuit potential. The determinations were carried out at a scan rate of 0.005 Vs^{-1}. The Tafel slopes, corrosion potential (E_{Corr}) and current (I_{Corr}) values were determined.

Surface Analysis by FTIR Spectroscopy

MS specimens immersed for one day in various test solutions were taken away and dried. The film produced on the metal surface was carefully removed and mixed scrupulously with KBr, so as to make it homogeneous. The FTIR spectra were carried out in a Perkin–Elmer–1600 spectrophotometer.

Surface analysis by Atomic Force Microscopy

AFM is the most versatile and powerful microscopy whereby the sample surface was scanned by a fine tip to find out surface morphology and properties to generate a 3D surface image. Besides imaging surfaces with nanometer resolution, the AFM was capable of determining surface roughness, probing local changes in friction, calculating surface forces and assessing local elasticity changes over a sample surface.

AFM uses a cantilever with a very sharp tip which interacts with the sample surface. To acquire the image resolution, AFMs can generally measure the vertical and lateral cantilever deflections by means of the optical lever. The optical lever operates by reflecting a laser beam off the cantilever. The reflected laser beam hits a position-sensitive photo detector. The differences between the segments of photo-detector signals specify the laser spot position on the detector and thus the angular deflections of the cantilever

RESULTS AND DISCUSSION

Analysis of Results of Weight Loss Study

The experimental results obtained from weight loss studies for different inhibitor concentrations for the MS corrosion in H_2SO_4 for one-day immersion at pH-4 are given in table 1. TU inhibits the corrosion of MS. As the concentration of TU increases, the IE increases. 250 ppm of Thiourea alone gives 55 % IE Table I (a). 250 ppm of L-Phenylalanine alone gives 38 % IE only Table 1 (b). In order to increase the IE, TU is combined with 25 ppm of Zn^{2+}, the IE increases with increase in the TU concentration, 25 ppm Zn^{2+} has 10 % IE and 250 ppm TU have 55 % IE. The combination of 250 ppm TU and 25 ppm Zn^{2+} shows 82%.

To increase the IE, TU- Zn^{2+} is combined with different concentrations of L-Phenylalanine. It is found that when L-Phenylalanine is added, the IE of TU-Zn^{2+} increases. The increase in IE is more pronounced at 250 ppm of L-Phenylalanine . The combination of 100 ppm TU, 25 ppm Zn^{2+} and 250 ppm L-Phenylalanine shows 95% (Table 1 c). Therefore, this ternary combination better IE than the individual inhibitors (Abdel-Fatah 2012; Ridhwan *et al.* 2012;

Umamathi *et al*. 2008). This suggests that the synergistic effect exists between TU, Zn^{2+} and L-Phenylalanine (Gowri *et al*. 2013; Manimaran *et al* 2012; Zhao and Mu 1999). Due to synergism, inhibition efficiency increases and corrosion rate decreases (Thiraviyam *et al.* 2012). That is, the system passes from active to passive region (Rao *et al*. 2011).

Table 1: Corrosion Rates (CR) and Inhibition Efficiencies (IE) Different Inhibitors System in Controlling the Corrosion of MS Immersed in H_2SO_4 Solution at pH-4 Obtained by Weight Loss Method.

Table 1: (a) TU and Zn^{2+}

TU ppm	Zn^{2+} 0 ppm		Zn^{2+} 25ppm	
	IE %	CR mm/y	IE %	CR mm/y
0	---	0.1947	10	0.1762
50	38	0.1205	55	0.0881
100	45	0.1113	65	0.0672
150	48	0.1020	74	0.0510
200	50	0.0974	80	0.0394
250	55	0.0881	82	0.0348

Table 1: (b) L-Phenylalanine

L-Phenylalanine ppm	IE %
50	30
100	32
150	34
200	36
250	38

Table 1 (c): TU and L-Phenylalanine

TU ppm	Zn^{2+} ppm	L-Phenylalanine ppm	Corrosion Rate mm/y	I.E %
0	0	0	0.1947	---
0	25	0	0.1762	10
100	25	50	0.02087	89
100	25	100	0.01855	91
100	25	150	0.01623	92
100	25	200	0.01391	93
100	25	250	0.00927	95

Analysis of Potentiodynamic Polarization Study

Potentiodynamic polarization study is used to validate the corrosion behavior and also used to study the kinetics of the cathodic and anodic reactions (Helal and Badawy 2011; Mary *et al*. 2015).

Figure (1) depicts the potentiodynamic polarization curves of MS immersed in H_2SO_4 solution at pH-4 containing 100 ppm of TU, 25 ppm of Zn^{2+} and 250 ppm of L-Phenylalanine. The corrosion parameters are presented in Table 2. In the presence of inhibitors, the corrosion potential shifted to cathodic side (from -598 mV to -601 mV vs SCE). But the shift is not very much. The largest shift evidenced by this inhibitor system is 3mV. Therefore, it is ensured that this system functions as a mixed type inhibitor (Hebbar *et al*. 2014; Ashassi-Sorkhabi *et al*. 2011). Simultaneously, in Simultaneously, in the presence of the inhibitor system, the corrosion current decreases from 2.394×10^{-6} A/cm^2 to 5.205×10^{-7}A/cm^2 and LPR value increases from 16724.9 ohm cm^2 to 723439.8 ohm cm^2. LPR value increased with the decrease in corrosion current density indicates the adsorption of the inhibitor on the metal surface to block the active sites and inhibit corrosion and diminishes the corrosion rate with the protective film formation on the metal surface (Selvarani *et al*. 2004; Kavitha and Manjula 2014).

a) pH-4 H_2S0_4; b) pH-4 H_2S0_4+TU (100 ppm)+Zn^{2+} (25 ppm)+L-Phenylalanine (250 ppm)

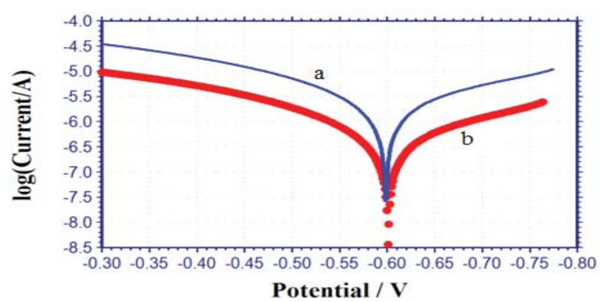


Fig. 1: Polarization Curves of MS Immersed in Various Test Solutions

Table 2: Corrosion Parameters of MS Immersed in H_2SO_4 Solution at pH-4 in the Absence and Presence of Inhibitor System TU (100 ppm) and Zn^{2+}(25 ppm)–L-Phenylalanine(250 ppm) Obtained by Polarization Method

TU ppm	Zn^{2+} ppm	L-Phenylalanine ppm	E_{corr} mV vs. SCE	b_c mV/ decade	b_a mV/ decade	LPR ohm cm^2	I_{corr} A/cm^2
0	0	0	-598	205	167	16724.9	2.394×10^{-6}
100	25	250	-601	196	155	723439.8	5.205×10^{-7}

Analysis of FTIR Spectra

FTIR spectrum is used to resolve the bonding type and the nature of inhibitors adsorbed on the metal surface (Sangeetha *et al.* 2012; Ruba Helen Florence *et al.* 2005; Karthik *et al.* 2015). Fig. (2a) shows the FTIR spectrum (KBr) of pure TU-. It is inferred from the figure that the C=O and C–N stretching frequency emerge respectively at 1594.55 cm^{-1} and 1175.01 cm^{-1}. The N–H stretching and bending frequencies emerge at 3415.60 cm^{-1} and 1474.47 cm^{-1} respectively. The C=O, C-N and N-H stretching frequency emerge respectively at 1732.92 cm^{-1}, 1198.30 cm^{-1} and 3410.43 cm^{-1} in the FTIR spectrum (KBr) of pure L- Phenylalanine(Fig. 2b).

Fig. 2(c) shows the FTIR spectrum of the film formed on the metal surface following immersion in H_2SO_4 solution at pH-4 containing TU (100 ppm) and Zn^{2+} (25 ppm) and 250 ppm of L-Phenylalanine. It is evident from the figure that The C=S stretching frequency has shifted to 1593.55 cm^{-1}. The NH stretching frequency shifted to 3401.51 cm^{-1}. The C-N stretching frequency shifted to 1383.45 cm^{-1}. The peak at 765.07 cm^{-1} is due to Zn–O stretching. This implies that TU and L-Phenylalanine coordinated with Fe^{2+}, through their polar groups resulting in the formation of Thiourea-Fe^{2+} complex and L- Phenylalanine- Fe^{2+} complex and $Zn(OH)_2$ formed on the metal surface(Epshiba *et al* 2017 ; Srimathi *et al.* 2014). This complex inhibits the corrosion.

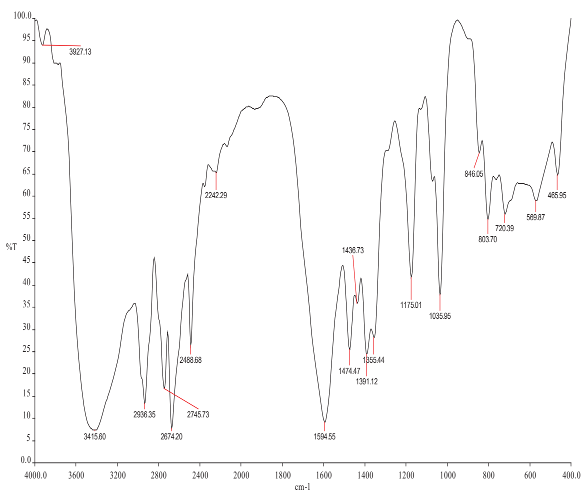


Fig. 2 (a) Pure TU

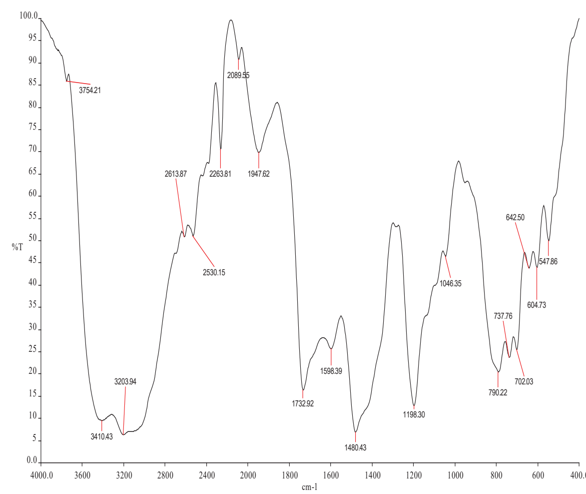


Fig. 2 (b) Pure L-Phenylalanine

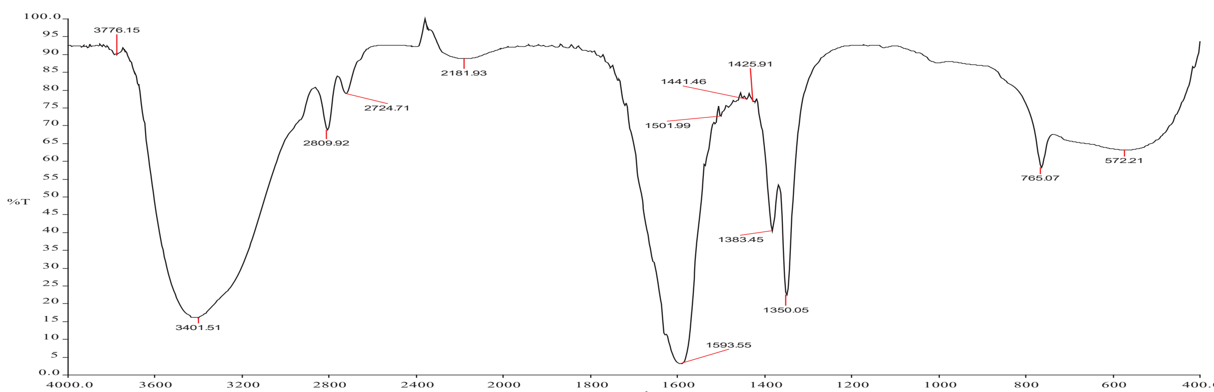


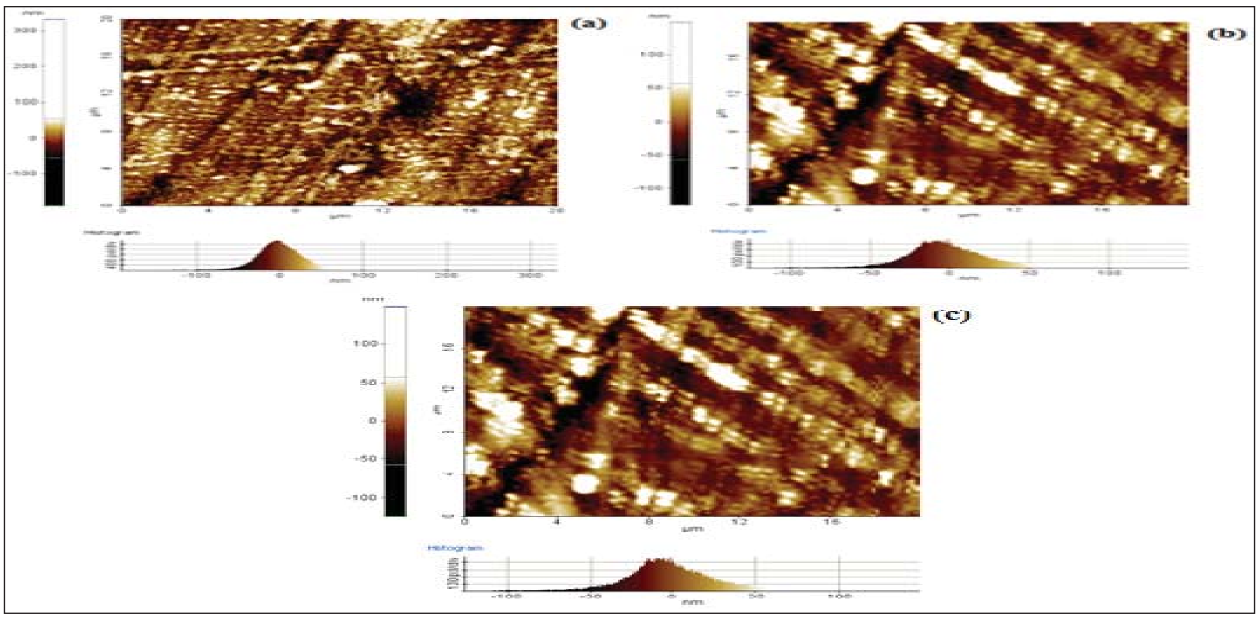
Fig. 2 (c) Film Formed on the Metal Surface after Immersion in Sulphuric Acid Solution at pH-4 Containing TU (100 ppm) and Zn^{2+}(25 ppm)+L-Phenylalanine(250 ppm)

Fig. (2) FTIR Spectra

Atomic Force Microscopy Characterization

Atomic Force Microscopy imaging is a very informative research method and measures the roughness of a sample surface at a high resolution in the order of fractions of a nanometer (Fouda *et al*. 2014; Singh & Quraishi 2011; Wang *et al*. 2011; Satapathy *et al*. 2009). The two dimensional AFM images of the polished metal corroded metal surface and in the presence of inhibitors TU, Zn^{2+} and L-Phenylalanine are shown in Fig. 3 respectively.

The average roughness (R_a), root mean square roughness (R_q) and maximum peak-to-valley height (P-V) value for MS surface engrossed in the different environment is displayed in Table 3. It is inferred from the table that the polished MS surface R_q, R_a and P-V height values that shows a more homogeneous surface are respectively 26.351 nm, 21.327 nm and 129.754 nm. The slight roughness noted on the polished MS surface is due to the atmospheric corrosion. The R_q, R_a and P-V height values for the MS surface immersed in H_2S0_4 solution at pH-4 are respectively 152 nm, 132 nm and 584 nm suggesting that MS surface in H_2SO_4 solution at pH-4 is severely corroded. But in the presence of TU, Zn^{2+} and L-Phenylalanine smoother surface was obtained and the R_q, R_a and P-V height values are decreased to 27.572 nm, 21.058 nm and 133.520 nm respectively. The reduction of these parameters established that MS surface becomes smoothened due to the deposition of inhibitors on the metal surface. The surface smoothness is caused by the hard protective film formation containing TU-Fe^{2+}, L-Phenylalanine-Fe^{2+} complex and $Zn(OH)_2$ on the metal surface thus retarding the mild steel corrosion (Sahayaraja & Rajendran 2012).



Before immersion in pH-4 H_2S0_4; b) After one day immersion in pH-4 H_2S0_4 c) After one day immersion in pH-4 H_2S0_4+TU (100 ppm) + Zn^{2+} (25 ppm)+ L-Phenylalanine (250 ppm)

Fig. (3): 2D AFM Images and Topography of the MS Surface

Table 3: AFM Data for MS Surface Immersed in Inhibited and Uninhibited Environment

Sample	RMS (R_q) Roughness (nm)	Average Roughness (Ra) (nm)	Maximum peak-to-valley Height (P-V) (nm)
Polished MS	26.351	21.327	129.754
MS immersed in H_2SO_4solution at pH-4	152	132	584
MS immersed in H_2SO_4 solution at pH-4 containing 100 ppm of Thiourea and 25 ppm of Zn^{2+} + 250 ppm of L-Phenylalanine	27.572	21.058	133.520

CONCLUSIONS

The inhibitor formulation containing 25 ppm Zn^{2+}, 100 ppm TU and 250 ppm L-Phenylalanine showed 95 % inhibition efficiency. Polarization study showed this formulation as a mixed inhibitor. FTIR spectra exposed the presence of Fe^{2+}-TU, Fe^{2+}-L-Phenylalanine complex and $Zn(OH)_2$ in protective film. AFM images pointed out the protective layer formation on the metal surface and its surface methodology.

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