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Corrosion Inhibition Of Mild Steel In Acid Solution By Thiourea- Zn^{2+}- L-Alanine System

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Abstract: The inhibition efficiency (IE) of Thiourea in combination with Zn^{2+} and L-Alanine on the corrosion of Mild steel in sulphuric acid at pH-4 was investigated by weight loss and electrochemical techniques. The ternary system, Thiourea (100 ppm) – Zn^{2+} (25 ppm) – L- Alanine (250ppm) has 91 % IE. IE values calculated from weight loss studies. Polarization study reveals that Thiourea -Zn^{2+}-L-Alanine system functions as a mixed - type inhibitor. The mechanistic aspects of corrosion inhibition have been studied using polarization study. AC impedance spectra reveal that a protective film is formed on the metal surface. The surface morphology of the protective film on the metal surface was analyzed by FTIR and SEM analysis.
Keywords: Corrosion Inhibition, Mild steel, Thiourea, L-Alanine, Potentiodynamic Polarization, FTIR, SEM.

INTRODUCTION

Corrosion inhibition of mild steel is a matter of theoretical as well as practical importance [1]. 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 hetero cyclic compounds containing N, S, O, & P have been reported as inhibitors [2-6].A large number of organic compounds has been used as corrosion inhibitors for mild steel and most of them are highly toxic to both human beings and environment. Due to the increasing environmental awareness and the negative effects of some chemicals, research activities in recent times are geared towards developing the less toxic and environmentally safe corrosion inhibitors [7-12]. Among these, thiourea and its derivatives have been investigated extensively. These are polar molecules in which S atom having permanent – ve charge and N atom have + ve charge. As the molecule approaches the electrode surface the electric field of double layer increases the polarization of molecule and induces additional charges on S and N atoms, a condition that enhance the adsorption of molecule [13].

This paper reports the corrosion behavior of Mild steel in sulphuric acid solution at pH-4 and the inhibition of corrosion of Mild steel by Thiourea- Zn^{2+}-L- Alanine system. The corrosion inhibition efficiency was calculated using weight loss studies. The mechanistic aspect of corrosion inhibition was studied by polarization studies.

The protective film formed on the metal surface characterized with the help of AC impedance. The surface morphology has been analyzed by FTIR and SEM.

EXPERIMENTAL

Preparation 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.

Weight – 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 [14]. The weight of the specimens before and after immersion were determined using a balance, Shimadzu AY62 model.

Then the Inhibition Efficiency was calculated using the equation

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

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,

$$CR = 87.6\ W/DAT\ mm/y$$

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

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 (I_{Corr}) and corrosion potential (E_{Corr}) values were calculated. During the polarization study, the scan rate (V/s) was 0.005; Hold time at E_f (s) was zero and quiet time (s) was 2.

AC impedance spectra

A CHI 660A electrochemical impedance analyzer model was used to record AC impedance measurements. 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 for various frequencies. The R_t (charge transfer resistance) and C_{dl} (double layer capacitance) values were calculated.

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 analytical techniques.

FTIR spectra:

The FTIR spectra were recorded in a Perkin –Elmer– 1600 spectrophotometer. The film formed on the metal surface was carefully removed and thoroughly mixed with KBr, so as to make it uniform throughout.

Scanning Electron Microscopy (SEM)

SEM (HITACHI S-3000H) provides a pictorial representation in the surface to understand the nature of the surface film in the absence and presence of inhibitors and extent of corrosion of mild steel. The SEM micrographs of the surface are examined.

RESULTS AND DISCUSSION

Weight loss method

The calculated corrosion inhibition efficiency (IE) and corrosion rates (CR) of Thiourea and Zn^{2+} and Thiourea, Zn^{2+} and L-Alanine in combination have been evaluated in sulphuric acid medium at pH-4 by weight loss technique and the results are summarized in Table I(a) to Table I (c).

Table 1 (a) ; Corrosion rates (CR) of mild steel immersed in sulphuric acid medium at pH-4 and the inhibition efficiencies (IE) obtained by weight loss method.

Inhibitor system: Thiourea + 0 ppm of Zn^{2+} Immersion period: 1 day

Thiourea ppm	Zn^{2+} ppm	Corrosion Rate mm/y	I.E %
0	0	0.1947	---
50	0	0.1205	38
100	0	.0.1113	45
150	0	0.1020	48
200	0	0.0974	50
250	0	0.0881	55

Table 1 (b); Corrosion rates (CR) of mild steel immersed in sulphuric acid medium at pH-4 and the inhibition efficiencies (IE) obtained by weight loss method.

Inhibitor system: Thiourea + 25 ppm of Zn^{2+} Immersion period: 1 day

Thiourea ppm	Zn^{2+} ppm	Corrosion Rate mm/y	I.E %
0	0	0.1947	---
0	25	0.1762	10
50	25	0.0881	55
100	25	0.0672	65
150	25	0.0510	74
200	25	0.0394	80
250	25	0.0348	82

Table 1(c); Corrosion rates (CR) of mild steel immersed in aqueous solution (pH4) and the inhibition efficiencies (IE) obtained by weight loss method.

Inhibitor system: 100 ppm Thiourea + 25 ppm of Zn^{2+} + L- Alanine Immersion period: 1 day

Thiourea ppm	Zn^{2+} ppm	L Alanine ppm	Corrosion Rate mm/y	I.E %
0	0	0	0.1947	---
0	25	0	0.1762	10
100	25	50	0.0301	84
100	25	100	0.0278	86
100	25	150	0.0231	88
100	25	200	0.02087	89
100	25	250	0.01855	91

From Table 1(a) it is clear that 250 ppm of Thiourea alone shows 55% IE. This indicates the ability of Thiourea to be a good corrosion inhibitor. But combination of 250 ppm of Thiourea and 25 ppm Zn^{2+} shows 82% IE. The IE is found to be enhanced in the **p**resence of Zn^{2+} ion. This shows that synergistic effect exist between Thiourea and Zn^{2+} [15 -17]. But when L- Alanine is added to the

combination of 100 ppm Thiourea, 25 ppm Zn^{2+} , the IE again increases. As the concentration of

L-Alanine increases, IE also increases. So 100 ppm of TU, 25ppm of Zn^{2+} and 250 ppm of

L-Alanine shows 91% IE.

Analysis 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 1 .

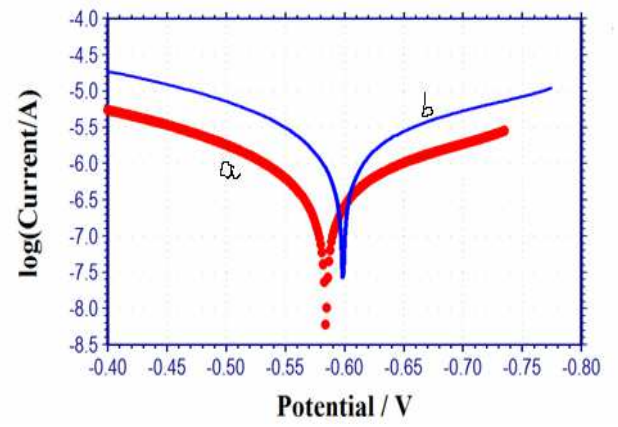

Fig 1 Polarization curves of mild steel immersed in various test solutions
a) Sulphuric acid media at pH-4
b) Sulphuric acid media at pH-4 containing 100 ppm of Thiourea + 25 ppm of Zn^{2+} +250 ppm of L-Alanine .

The corrosion parameters such as corrosion potential (E_{Corr}), Tafel slopes (anodic slope b_a and Cathodic slope b_c), linear polarization resistance and corrosion current (I_{Corr}) values were calculated are given in Table 2.

When Mild steel immersed in sulphuric acid media at pH-4, the corrosion potential is -598 Vs saturated calomel electrode (SCE). The corrosion current is $2.394x10^{-6}$ A/cm$^{2.}$ .But when Thiourea (100 ppm), Zn^{2+} (25 ppm) and 250 ppm of L-Alanine are added to the above system the corrosion potential is shifted to the anodic side (from -598 mV to -584 mV). This suggests that the anodic reaction is controlled predominantly. However the shift is not very much. Therefore it is concluded that the system functions as a mixed type inhibitor. More over in presence of the inhibitor system, the corrosion current decreases from $2.394x10^{-6}$ A/cm^2 to 6.348×10^{-7} A/cm^2 and LPR value increases from 16724.9 ohm cm^2 to 58957.7 ohm cm^2 .These observations indicate the formation of protective film on the metal surface [18-20].

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

Thiourea ppm	Zn^{2+} ppm	Alanine ppm	Ecorr mV vs. SCE	b_c mV/decade	b_a mV/decade	LPR ohm cm^2	Icorr A/cm^2
0	0	0	-598	205	167	16724.9	$2.394x10^{-6}$
100	25	250	-584	189	158	58957.7	6.348×10^{-7}

AC impedance spectra

AC impedance spectra [electrochemical impedance spectra] have been used to confirm the formation of protective film on the metal surface [21-23]. The AC impedance spectra of mild steel immersed in various test solutions are shown in Fig.2 (Nyquist plots) and Fig.3 (Bode plots). The impedance parameters namely charge transfer resistance ($R_{t)}$ double layer capacitance (C_{dl}) and impedance log(z/ohm) are given in Table 3. If a protective film is formed on the metal surface, R_t value increases and the C_{dl} value decreases.

When Mild steel is immersed in sulphuric acid medium at pH-4, R_t value is 4857ohm cm^2 and C_{dl} value is $3.9489x10^{-9}$ F/ cm$^{2.}$ When 100 ppm of Thiourea ,25 ppm of Zn^{2+} and 250 ppm of L-Alanine are added R_t value again increases from 4857ohm cm^2 to 15389 ohm cm^2 and the C_{dl} decreases from $3.9489x10^{-9}$ F/ cm^2 to $1.2463 x10^{-9}$ F/ cm^2. This suggests that a protective film is formed on the surface of the metal. Impedance value increases from 3.792 to 4.256 log(z/ohm). This accounts for the very high IE of Thiourea_ Zn^{2+} - L-Alanine system.

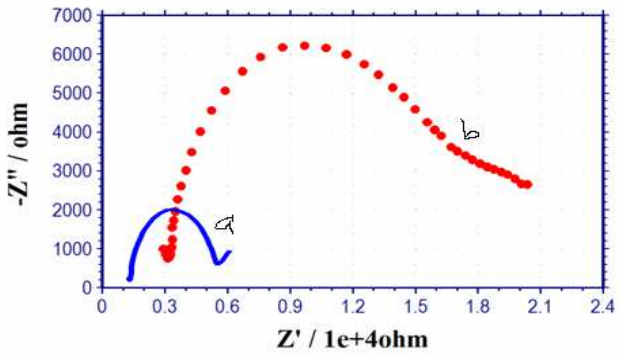

Fig. (2). AC impedance spectra (Nyquist plots) of Mild steel immersed in various test solutions.
a) Sulphuric acid media at pH -4
b) Sulphuric acid media at pH-4. containing 250 ppm of Thiourea, 25 ppm of Zn^{2+} and 250 ppm of Alanine.

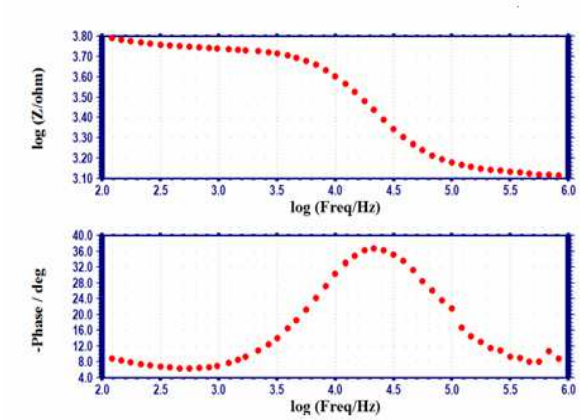

Fig.3 (a).

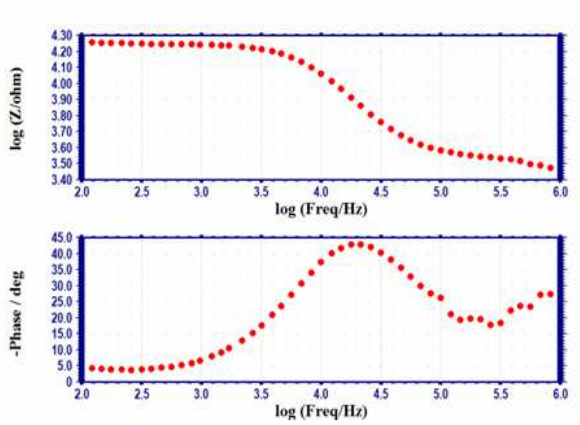

Fig.3 (b).

Fig.3 (a). Ac impedance spectra of mild steel(Bode plot) immersed in sulphuric acid medium at pH-4. (Blank)
Fig.3(b). Ac impedance spectra of mild steel (Bode plot) immersed in sulphuric acid at pH-4 containing 100 ppm of Thiourea +25 ppm of Zn^{2+}+ 250 ppm of L-Alanine

Table 3 : Impedance Parameters of Mild Steel in sulphuric acid medium at pH-4 in the absence and presence of inhibitor obtained by AC Impedance Method

Thiourea (ppm)	Zn^{2+} (ppm)	L-Alanine ppm	R_t Ohm cm^2	C_{dl} F/cm^2	Impedance log(z/ohm)
0	0	0	4857	$3.9489x10^{-9}$	3.792
100	25	250	15389	$1.2463\ x10^{-9}$	4.256

Analysis of FTIR spectra:

The FTIR spectrum of pure Thiourea and pure L-Alanine is shown in Fig.4 (a) and 4 (b) respectively.. The characteristic absorption peaks of these two compounds are very well seen in the spectra.FTIR spectrum of the inhibitor system (Thiourea – Zn^{2+} – L-Alanine) in sulphuric solution at pH-4 on mild steel is given in Fig 4(c) on The shifts in the frequencies of the absorption peaks clearly indicate the formation of complexes of the inhibitors with Fe^{2+}, and Zn^{2+} which are adhered on the surface of the specimen during immersion [24].

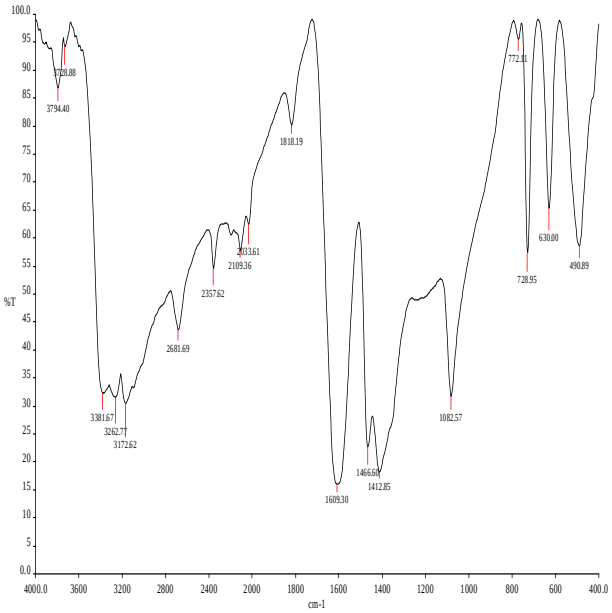

Fig.4 (a): FTIR spectrum of pure Thiourea

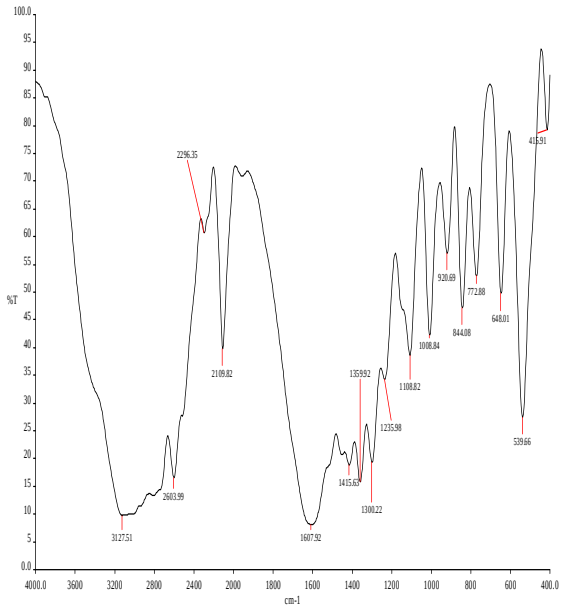

Fig.4 (b): FTIR spectrum of pure L-Alanine

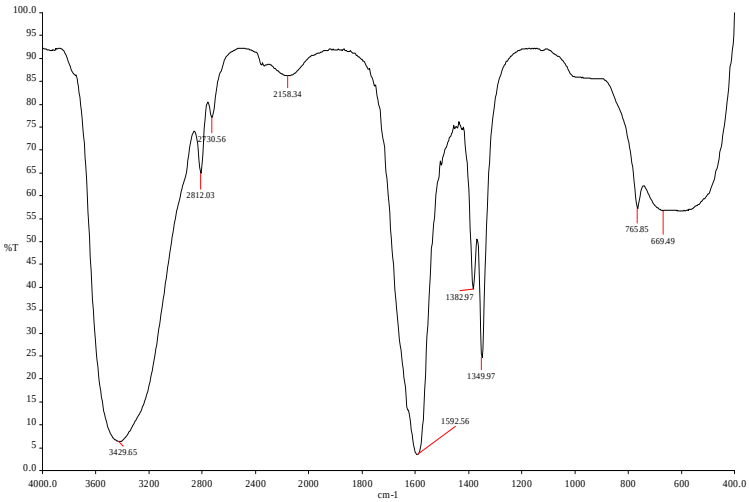

Fig.4 (a): FTIR spectrum of 100 ppm of Thiourea, 25 ppm of Zn^{2+} and 250 ppm of L-Alanine.

Scanning Electron Microscopy (SEM):

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 (X 500) of polished Mild Steel surface (control) in Fig. 5. (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 500) of Mild steel specimen immersed in the sulphuric acid medi at pH-4 for one day in the absence and presence of inhibitor system are shown in Fig.5. (b) and 5(c) respectively.

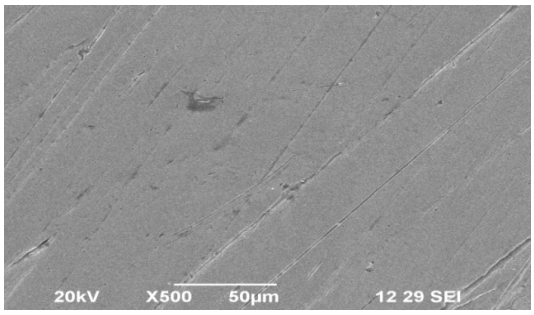

Fig. 5. (a)

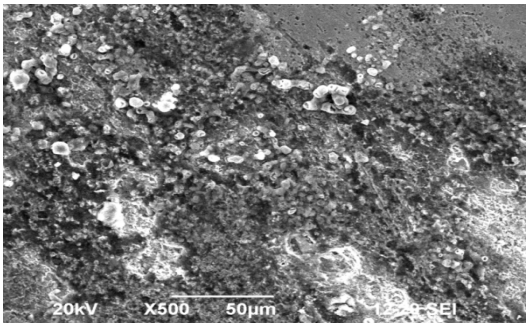

Fig. 5. (b)

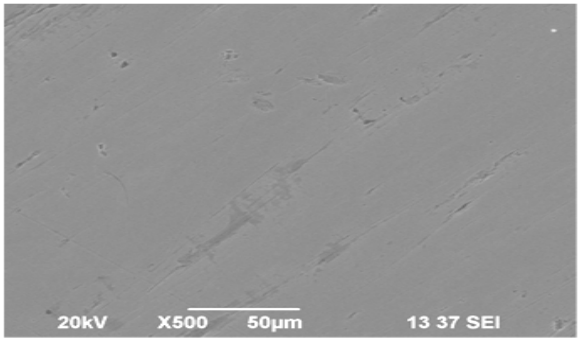

Fig 5 (c)

Fig 5 SEM micrographs of Mild steel surface (Magnification – X 500)
a) Polished Carbon steel (control), (b) Mild steel immersed in sulphuric acid media at pH-4,
(c) Mild steel immersed in Sulphuric acid media at pH-4 containing Thiourea (100 ppm) + Zn^{2+} (25 ppm) + 250 ppm of L-Alanine;

The SEM micrographs of Mild steel surface immersed in sulphuric acid media at pH-4 in Fig.5. **(b) s**hows the roughness of the metal surface which indicates the corrosion of mild steel in Sulphuric acid media. Fig 5(c) indicates that in the presence of 100 ppm Thiourea and 25 ppm Zn^{2+} and 250 ppm of L-Alanine in sulphuric acid media at pH-4, the surface coverage again increases which in turn results in the formation of insoluble complex on the surface of the metal. In the presence of Thiourea, Zn^{2+} and L-Alanine, the surface is covered by a thin layer of inhibitors which effectively control the dissolution of Mild steel [25-29].

CONCLUSIONS

The present study leads to the following conclusions:

1. The inhibition efficiency (IE) of Thiourea in controlling corrosion of Mild steel immersed in

Sulphuric acid media at pH-4 in the absence and presence of Zn^{2+} and L-Alanine has been evaluated by weight loss method. The formulation consisting of 100 ppm Thiourea, 25 ppm Zn^{2+} and 250 ppm of L-Alanine has 91% corrosion inhibition efficiency. Polarization study reveals that Thiourea – Zn^{2+} - L-Alanine system behaves as an mixed type inhibitor.. AC Impedance spectra reveal that protective film is formed on the metal surface. FTIR and SEM confirms the formation of protective layer on the metal surface.

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