Corrosion Behaviour of Mild Steel In The Presence Of TIPA and Zn^{2+}

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Abstract: *The inhibition efficiency of the formulation consisting of Triisopropanol amine (TIPA) and Zn^{2+} in controlling the corrosion of mild steel in aqueous solution containing 60 ppm Cl^{-} has been evaluated by the weight loss method. The formulation consisting of 100 ppm TIPA, and 50 pm Zn^{2+} has 62.5% inhibition efficiency TIPA alone has 46% efficiency. The nature of the protective film has been analyzed by polarization study, AC impedance spectra. A suitable mechanism of corrosion inhibition is proposed based on the results obtained from the weight loss method, polarized study, AC impedance spectra and FTIR spectra.*
Keywords: *Synergism, TIPA, Polarization study, AC impedance and FTIR spectra.*

I.   Introduction

Mild steel is widely used as a constitutional material in many industries due to its good mechanical properties of low cost. The corrosion of mild steel is of fundamental academic and industries concern that has received a considerable amount of attention [1-5]. Acid picking paths are employed to remove in desirable scale from the surface of the metals [6-9]. Once the scale is removes the acid is then free for further attack on the metal surface. The use of inhibitors is one of the most practical methods for protection against corrosion especially in acidic media.

A survey of literature reveals that the applicability of organic compounds as corrosion inhibitors for mild steel in acidic media has been recognized for a long time [10-12] compounds studies as inhibitors include triazole derivatives. These compounds can adsorb on the mild steel surface and block the active sites decreasing the corrosion rate [13-15].

The present work is undertaken

(i)   To evaluate the inhibition efficiency of TIPA (Triisopropanolamine) in controlling corrosion of carbon steel in aqueous solution containing 60ppmcl^{-}

(ii) To analyze protective film by FTIR and

(iii) To make use of polarization study and AC impedance spectra to know the mechanistic aspects of corrosion inhibition.

1.1. Experimental procedure

1.1.1. Preparation of specimens

Carbon steel specimens were chosen from the same sheet of the following composition 0.1 Percent C, 0.026 percent S, 0.06 percent P, 0.4 percent Mn and the balance Fe. Carbon steel specimen of the dimensions $1.0 \times 4.0 \times 0.2$ cm were polished to more finish degreased with Acetone and used for mass loss and surface examination studies. The environment chosen is an aqueous solution containing 60 ppm Cl^{-}

1.1.2. Weight loss study

The weighed specimen in triplicate were suspended by means of glass hooks in 100ml beakers containing 100ml of double distilled water in various concentration of inhibitors in the presence and absence of Zn^{2+} for 1 day of immersion. After 1 day of immersion the specimens were taken out, washed in running water dried and weighed. From the change in weights of the specimen corrosion rates were calculated using the following relationship.

$$\text{Corrosion rate} = \frac{\text{Loss in weight (mg)}}{\text{Surface area of the specimen (dm}^2) \times \text{Period of immersion (days)}}$$

Corrosion inhibition efficiency (IE) was then calculated using the equation

$$IE = 100[1 - W_2 / W_1] \%$$

Where W_1=corrosion rate in the absence of the inhibitors and W_2=corrosion rate in the presence of the inhibitors

1.1.3. Potentiodymanic polarization

Polarization studies carried out in a CHI electrochemical workstation with impedance, Model 660 A, a three electrode cell assembly was used. The working electrode was one of the three metals. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode from the polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) and tafel slopes (anodic b_a and cathodic b_c) were calculated.

1.1.4. AC impedance measurements

EG and G electrochemical impedance analyzer model 6310 was used to record AC impedance measurements. A three electrode cell assembly was used. The working electrode was a rectangular specimen of carbon steel with one face of the electrode of constant $1cm^2$ area exposed. A rectangular platinum foil was used as the counter electrodes. A time interval of 5 to 10minutes was given for the system to attain a steady state open circuit potential. Then over this steady state potential, an AC potential of 10 mV was superimposed. The AC frequency was varied from 100 MHz to 100 KHz. The real part (Z') and imaginary part (Z") of the cell impedance were measured in Ohms for frequencies. The R_t (Charge transfer resistance) and C_{dl} (double layer capacitance) values were calculated. C_{dl} values were calculated using the following relationship.

$C_{dl} = 1/2 \times 3.14 \times f_{max} \times R_t$

1.1.5. FTIR

There spectra were recorded in a Perkin-Elmer 1600 spectra photometer. The film was carefully removed, mixed thoroughly with KBr and made in to pellets and the FTIR spectra were recorded.

II.   RESULTS AND DISCUSSION

2.1. Weight loss study

The inhibition efficiencies (IE) of TIPA in controlling corrosion of carbon steel immersed in aqueous solution containing 60ppm of Cl$^-$ for one day in the presence of absence of Zn^{2+} obtained by weight loss are given in table (1-2). TIPA alone has some IE. Inhibition efficiency is more pronounced at 100 ppm of TIPA and 50 ppm of Zn^{2+} exits. For example 50 ppm of Zn^{2+} has 23% IE and 100 ppm of TIPA has 47% IE. However the formulation consisting of 100 ppm of TIPA and 50 ppm of Zn^{2+} shows 63% IE. It is observed as the concentration of TIPA increases the IE decreases. This is due to the fact that the protective film formed on the metal surface is broken and goes in to the solution.

TABLE 1. Corrosion rates of (CR mdd) carbon steel immersed in an aqueous solution containing 60 ppm of Cl$^-$ and the inhibition efficiencies (IE %) obtained by weight loss method (pH=8.2)

Cl$^-$ ppm	TIPA ppm	IE %	CR mdd
60	50	28	8.12
60	100	47	13.34
60	150	31	8.99
60	200	31	8.99
60	250	25	7.25

TABLE 2. Corrosion rates (CR mdd) carbon steel immersed in an aqueous solution containing 60 ppm Cl$^-$ and the inhibition efficiencies (IE%) obtained by weight loss method (pH=8.2)

Cl$^-$ ppm	TIPA ppm	Zn^{2+} ppm	IE %	CR mdd
60	0	0	-	29
60	0	50	23	6.67
60	50	50	18	5.04
60	100	5	63	18.13
60	150	50	38	10.8
60	200	50	34	10
60	250	50	18	5.22

2.2. Potentio static polarization study for TIPA- Zn^{2+} system

The corrosion parameters of carbon steel immersed in various test solution obtained by polarization study are given in table 3. The polarization curves are shown in figure 1.
When carbon steel is immersed in aqueous solution containing 60 ppm Cl$^-$, the corrosion potential is -611 mV versus saturated calomel electrode (SCE). The formulation containing of 100 ppm of TIPA and 50 ppm of Zn^{2+}

shifts the corrosion potential -595mV versus SCE. The corrosion current for aqueous solution containing 60 ppm of Cl^- is $7.923 \times 10^{-7} A/cm^2$. The corrosion current for formulation consisting of 60 ppm Cl^-, TIPA (100 ppm), Zn^{2+} (50 ppm) have decreased to 6.594×10^{-7}. The linear polarization resistance for aqueous solution containing 60 ppm Cl^- is 4.90×10^5 ohm cm^2. The LPR for formulation consisting of 60 ppm Cl^-, TIPA (100 ppm), Zn^{2+} (50 ppm) has increased to 5.55×10^5 ohm cm^2. This is due to the formation of a protective film formed on the metal surface.

TABLE 3. Corrosion parameters of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^- obtained from potentio dynamic polarization study

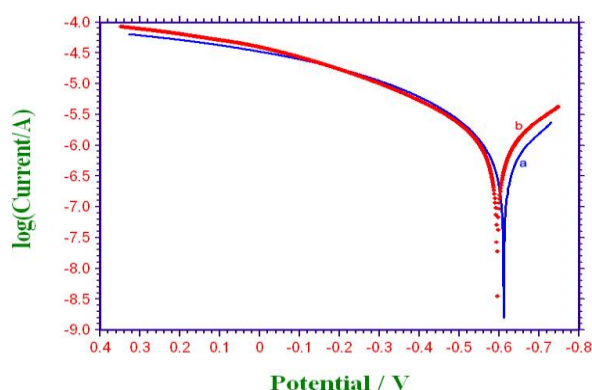| System	E_{corr} mV Vs SCE	b_a mV/decade	b_c mV/decade	LPR ohm cm^2	I_{Corr} A/cm^2
Aqueous solution containing 60 ppm Cl^-	-611	597	522	4.90×10^5	7.923×10^{-7}
Aqueous solution containing 60 ppm Cl^- +TIPA (100 ppm) + Zn^{2+} (50 ppm)	-595	594	592	5.55×10^5	6.594×10^{-7}

Fig 1. Polarization curves of mild steel immersed in various test solutions
a) 60 ppm Cl^- (Blank) b) TIPA (100 ppm) + Zn^{2+} (50 ppm)

TABLE 4. Corrosion parameters of carbon steel immersed in aqueous solution containing 60 ppm Cl^- obtained by AC impedance spectra.

System	R_t ohm cm^2	C_{dl} F/cm^2	Impedance [log(Z/ohm)]
Aqueous solution containing 60 ppm Cl^-	1359	8.094×10^{-10}	4.420
Aqueous solution containing 60 ppm Cl^- + TIPA (100 ppm) + Zn^{2+} (50 ppm)	1975	1.762×10^{-9}	4.461

2.3. AC impedance spectra

The AC impedance spectra of carbon steel immersed in aqueous solutions containing 60 ppm Cl^- in the absence and presence of inhibitors are shown in figure 2 (Nyquist plots) and figure 3 (Bode plots). The AC impedance parameters, namely charge transfer resistance (R_t) and double layer capacitance C_{dl} and log Z/ohm are calculated.

An aqueous solution containing 60 ppm of Cl^- has R_t value of 1359 ohm cm^2 and C_{dl} value of 8.094×10^{-10} F/cm^2. In the presence of TIPA and Zn^{2+} R_t value increased from 1359 ohm cm^2 to 1975 ohm cm^2. The C_{dl} decreases from $8.09 \times 10{-}10$ F/cm^2 to 1.762×10^{-9} F/cm^2. The impedance value increases from 4.420 to 4.461. This observation is shown in table 4 and suggests that a protective film is formed on the surface of the metal.
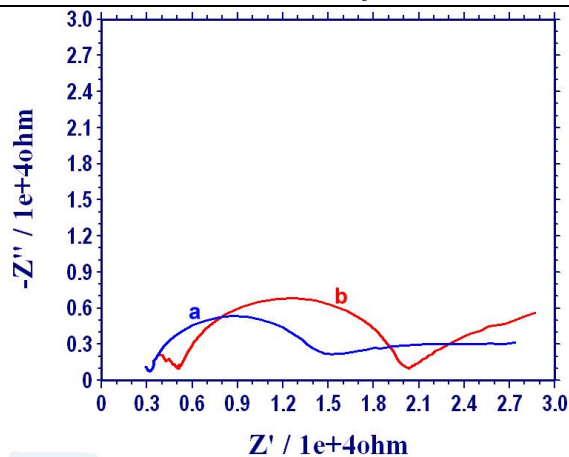
Fig 2. AC impedance spectra of mild steel immersed in various test solutions (Nyquist Plot)
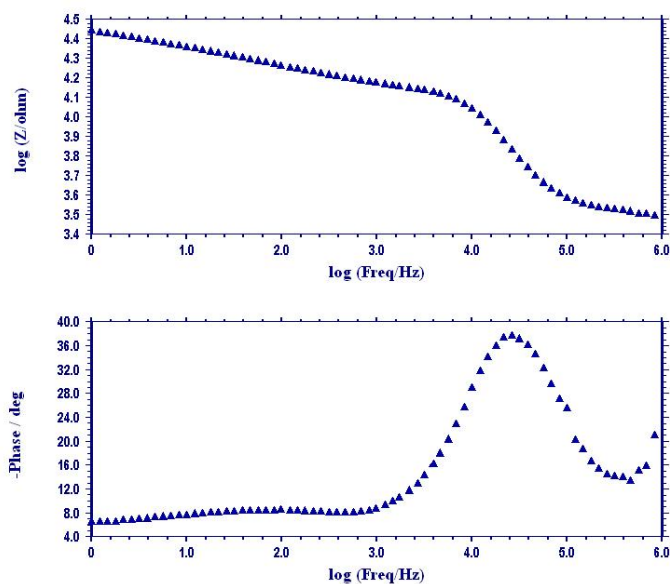a) 60 ppm Cl⁻ (Blank) b) TIPA (100 ppm) + Zn^{2+} (50 ppm)
b)

Fig 3a. AC impedance spectra of mild steel immersed in various test solutions (Bode Plot)
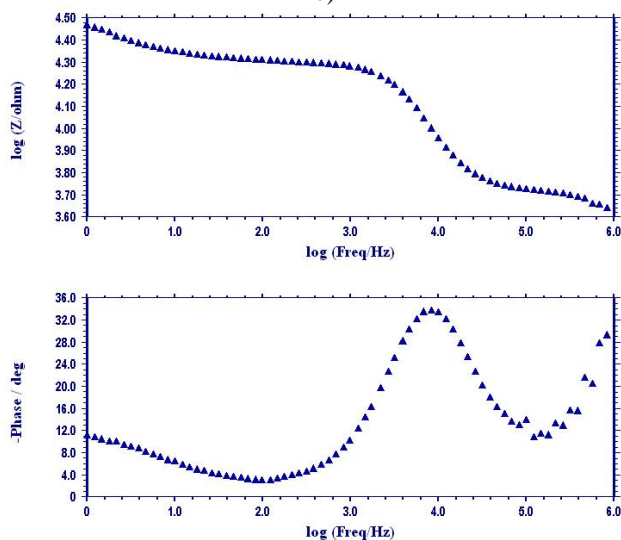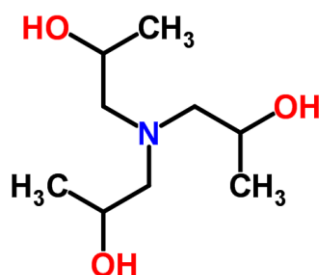a) 60 ppm Cl⁻(Blank)
b)

Fig 3b. AC impedance spectra of mild steel immersed in various test solutions (Bode Plot)
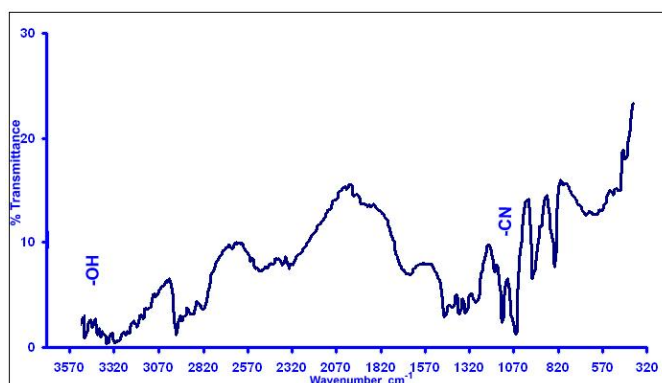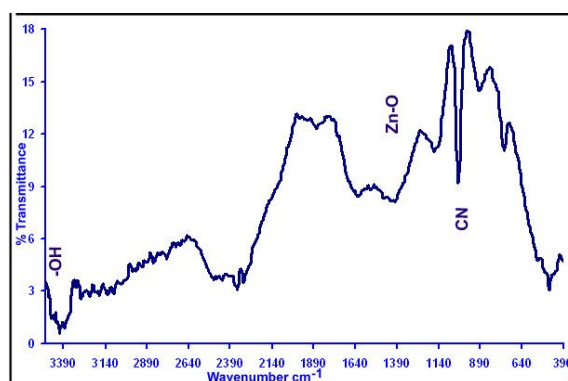a) TIPA (100 ppm) + Zn^{2+}(50 ppm)

2.4. FTIR spectra

Triisopropanolamine
Scheme 1.Molecular Structure of 1,1',1''-Nitrilotri(2-propanol)

FTIR spectrum of pure TIPA is shown in figure 4a. The –NH stretching and –OH stretching frequency have overlapped and appears at 3350 cm⁻¹. The –CN stretching frequency appears 1042 cm⁻¹. The FTIR spectra of film formed on the metal surface after immersion in solution containing 60 ppm Cl⁻, 100 ppm of TIPA and 50 ppm Zn²⁺ is shown in figure 4b. The –OH stretching frequency has shifted from 3350 cm⁻¹ to 3576 cm⁻¹. The –CN stretching frequency has shifted 1042 cm⁻¹ to 1064 cm⁻¹. This suggest that Fe²⁺ has coordination with TIPA through O atom of OH group and N atom –NH group resulting in the formation of Fe²⁺-TIPA complex on the metal surface. The peak at 1246 cm⁻¹ is due to Zn-O stretching frequency. The –OH stretching frequency appears at 3576 cm⁻¹. Hence it is inferred that Zn(OH)₂ is present on the metal surface [16-17].

Fig 4a. Pure TIPA

Fig 4b.Film formed on carbon steel after immersion in aqueous solution containing 100 ppm of TIPA + 50 ppm of Zn²⁺

2.5. Mechanism of Corrosion inhibition
Based on the above results, the following mechanism of corrosion inhibition is proposed

(i)   When the solution containing 60 ppm of Cl^-, 100 ppm of TIPA, 50 ppm of Zn^{2+} is prepared, there is formation of Zn^{2+}-TIPA complexes in solution.

(ii) When carbon steel is immersed in the solution, the Zn^{2+}-TIPA complexes diffuse from the bulk of the solution towards the metal surface.

(iii) On the metal surface, Zn^{2+}-TIPA complexes are converted in to Fe^{2+}-TIPA complexes on the anodic sites. Zn^{2+} is released.

(iv) Zn^{2+}-TIPA+ $Fe^{2+} \rightarrow Fe^{2+}$-TIPA+$Zn^{2+}$ the released Zn^{2+} combines with OH^- to form $Zn(OH)_2$ on the cathodic site.

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

III.   Conclusion

The present study leads to the following conclusions.

(i)   The formulation consisting of 100 ppm of TIPA, 50 ppm of Zn^{2+} has 63% IE.

(ii) Polarization study reveals that TIPA-Zn^{2+} system control anodic reaction predominantly.

(iii) AC impedance spectra reveal that a protective film is formed on the metal surface.

(iv) FTIR spectra reveal that the protective film consists of Fe^{2+}-TIPA complex and $Zn(OH)_2$

IV.   Acknowledgements

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