EFFECT OF CITRATE IONS ON THE ELECTROCHEMICAL BEHAVIOUR OF MILD STEEL IN TIPA – Zn^{2+} SYSTEM (TIPA=TRIISOPROPANOLAMINE)

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The inhibition efficiency (IE) of various concentrations of a TIPA(triisopropanolamine)-TSC(trisodium citrate)-Zn^{2+} system in controlling corrosion of mild steel immersed in aqueous solution containing 60 ppm Cl⁻ was evaluated by a weight loss study. The formulation consisting of 100 ppm of TIPA and 50 ppm of Zn^{2+} showed 62% inhibition efficiency. When TSC (250 ppm) is added the inhibition efficiency increases to 100%. In the presence of TSC has excellent inhibition efficiency. Polarization studies reveal that TIPA-TSC-Zn^{2+} function as an anodic inhibitor. AC impedance spectra suggest that a protective film is formed on the metal surface. FTIR spectra reveal that the protective film consists of Fe^{2+} - TIPA, Fe^{2+} - TSC complex and Zn(OH)$_2$.

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Introduction

Studies on the corrosion of metals in organic medium have attracted considerable interest in recent years due to their wide applications. It has been reported that the overvoltage for the cathodic reaction on metals in contact with such medium is lower than to the aqueous medium. Hence it causes accelerated, uniform and localized types of corrosion attack. It has been found earlier that the corrosion caused by the aqueous organic solvents can be effectively controlled by the use of corrosion inhibitors for a system can not only extend the life of the reaction vessels in use but could also enable the use of a less expense.[1-5]

Therefore, in this investigation, the authors have chosen mild steel to study corrosion inhibition, in contact with a very important aqueous organic medium petroleum having acetic acid and NaCl, Amines that are reported as good organic inhibitor for aqueous acid solutions have been used as inhibitor in this study. The aim of our study was to propose surface protection that will be able both to act in the corrosive medium having petroleum, and to have a tumble rule to chosen a best chemical structure for such mediums.

In previous work the mode of action of some alkyl amines to protect of mild steel was studied. It was shown that two intermediates adsorbed on the steel surface. Because these amines are different in attached groups, we choose to investigate the electrochemical corrosion behavior of carbon steel inhibited by amines with different structures.[6]

These organic compounds adsorb on the metal surface and suppress metal dissolution and reduction reactions. In most cases, it appears that adsorption inhibitors affect both the anodic and cathodic process although in many cases the effect is unequal.[7]

Materials and Methods

Sample Preparation

Carbon steel specimens (0.026% S, 0.067 % P, 0.4% Mn, 0.1% C and the rest iron) of the dimensions 1.0 cm x 4.0 cm x 0.2 cm were polished to mirror finish and degreased with Acetone and used for weight loss method.

Weight Loss Method

Mild steel specimens in triplicate were immersed in 100 ml of aqueous solution containing 60 ppm Cl⁻ and various concentrations of Triisopropanolamine in the presence and absence of Zn^{2+} (as ZnSO$_4$.7H$_2$O) for a period of one day. The corrosion products were cleaned with Clark's solution.[8] The weight of the specimens before and after immersion was determined using Shimadzu balance AY62. The corrosion inhibition efficiency was calculated with

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

Where W$_1$ is the corrosion rate in the absence of the inhibitor and W$_2$ is the corrosion rate in the presence of inhibitor. From the weight loss, the corrosion rates was calculated ρ- density of the metal is g cm^{-3}.

Electrochemical Study

Polarization studies were carried out using a CHI electro chemical impedance analyzer, model 660 A. A three electrode cell assembly was used. The working electrode was a rectangular specimen of mild steel with one face of electrode (1 cm^2 area) exposed and the rest shielded with red

lacquer. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode. Polarization curves were recorded using iR compensation. The results, such as tafel slopes and I_{corr}, E_{corr}, and LPR values were calculated. During the Polarization study, the scan rate (V/S) was 0.01, hold time at E f(s) was zero, and quit time (s) was 2.

AC impedance measurement

A time interval of 5 to 10 minutes was give for the system to attain a steady state open circuit potential. 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 various frequencies. The R_t(charge transfer resistance) and C_{dl} (double layer capacitance) were calculated. C_{dl} values were calculated by using the following relationship.

$$C_{dl} = \frac{1}{2\pi R_t f_{max}} \qquad (2)$$

FT-IR spectra

These spectra were recorded in a perki-Elmer 1600spectrophotometer. The film was carefully removed, mixed thoroughly with Kbr and made in to pellets and the FTIR spectra were recorded

Results and Discussion

Analysis of the Weight Loss Method

Corrosion rates (CR) of mild steel(MS) immersed in aqueous solution containing 60 ppm Cl⁻ in the absence and presence of inhibitors triisopropanolamine, Zn^{2+}, trisodium citrate are given in Table 1-3. The inhibition efficiencies (IE) are also given in this table. It is observed from table 1 that triisopropanolamine(TIPA) shows some inhibition efficiency of 47%. 100 ppm of TIPA and 50 ppm of Zn^{2+} shows 63% inhibition efficiency. After the addition of trisodium citrate(TSC) 250 ppm the increase in inhibition efficiency of the system (TIPA + TSC+ Zn^{2+}) is 100% IE.

Table 1. Corrosion rates of (CR mdd) mild 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) mild 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	Zn²⁺ ppm	IE %	CR mdd
60	0	0	-	29
60	0	50	23	6.67
60	50	50	18	5.04
60	100	50	63	18.13
60	150	50	38	10.8
60	200	50	34	10
60	250	50	18	5.22

Table 3. Corrosion rates (CR mdd) mild 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	Zn²⁺ ppm	TSC ppm	IE %	CR mdd
60	100	50	50	68.75	9.06
60	100	50	100	87.50	3.62
60	100	50	150	97.81	0.63
60	100	50	200	96.80	0.92
60	100	50	250	100	-

Influence of TSC on the inhibition efficiencies of TIPA

The inhibitory[17] and co-inhibitory effect[18] of trisodium citrate has been described recently. The influence of TSC on the inhibition efficiencies of TIPA + Zn^{2+} system is given in table 3. It is observed that as the concentration of TSC increases the IE increases. It is also observed that a synergistic effect exists between TSC and TIPA + Zn^{2+} system. For example 100 ppm of TIPA, 50 ppm of Zn^{2+} and 250 ppm of TSC has 100% IE. On the metal surface Fe^{2+}-TIPA complex and Fe^{2+}–TSC 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 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 TIPA-Zn^{2+} and TSC.

$Fe \rightarrow Fe^{2+} + 2e^-$ (Anodic reaction)

$Fe^{2+} + Zn^{2+}$-TIPA-TSC complex$\rightarrow Fe^{2+}$-TIPA+Fe^{2+}-TSC+

$$Zn^{2+}$$

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (Cathodic reaction)

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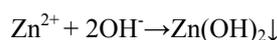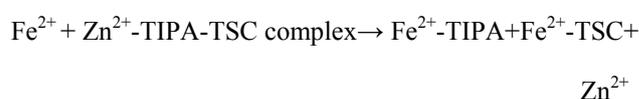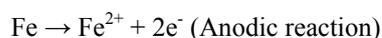
Corrosion Measurement

Polarization study has been to confirm the formation of protective film formed on the metal surface during corrosion inhibition process.[9-14] If a protective film is formed on the metal surface. The linear polarization resistance value (LPR) increases and the corrosion current value (I_{corr}) decreases.

The potentiodynamic polarization curves of mild steel immersed in aqueous solution containing 60 ppm Cl$^-$ in the absence and presence of inhibitors are shown in figure 1. The corrosion parameters are given in table 4. When mild steel was immersed in 60 ppm Cl$^-$ the corrosion potential was -583mV versus SCE. When TIPA (100 ppm), Zn^{2+} (50 ppm) and TSC (250 ppm) were added to the above system, the corrosion potential shifted to the noble side -436 mV versus SCE. This indicates that a film is formed on the anodic sites of the metal surface. This film controls the anodic reaction of metal dissolution by forming Fe^{2+}-TIPA, Fe^{2+}-TSC complex on the anodic sides of the metal surface. The formation of protective film on the metal surface is further supported by the fact that the anodic Tafel slope (b_a) increases from 170 to 197 mV. Further, the LPR value increases from 1.693 x 10^4 ohm cm^2 to 4.6 x 10^4 ohm cm^2. The corrosion current decreases from 1.873 x 10^{-6} A cm^{-2} to 7.54 x 10^{-7} A cm^{-2}. Thus Polarization study confirm the formation of a protective film on the metal surface

Table 4. Corrosion parameters of mild steel immersed in A obtained from polarization study

System	E_{corr} mV*	b_a, mV**	b_c mV**	*LPR* Ω cm^2	I_{corr} A cm^{-2}
A	-583	127	170	1.693 x 10^4	1.873x10^{-10}
A+B	-436	135	197	4.6 x 10^4	7.54x10^{-7}

A=Aqueous solution containing 60 ppm Cl$^-$; B= TIPA (100 ppm); Zn^{2+} (50 ppm); TSC (250 ppm); *mV vs SCE; ** mV in one decade.
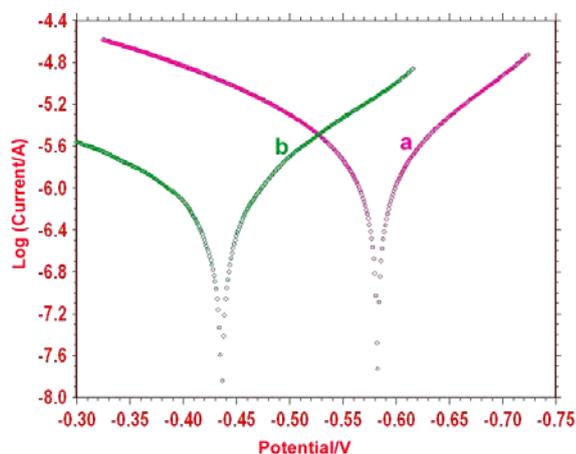
Figure 1. Polarization curves of MS is immersed in a) 60 ppm Cl$^-$ (Blank) b) TIPA (100 ppm) + Zn^{2+} (50 ppm) + TSC (250 ppm)

Analysis of AC impedance spectra

AC impedance spectra (electro chemical impedance spectra) have been used to confirm the formation of protective film on the metal surface. If a protective film is formed on the metal surface, charge transfer resistance (R_t) increases, double layer capacitance value (C_{dl}) decreases, and the impedance log (Z ohm^{-1}) value increases. The AC impedance spectra of mild steel immerse in an aqueous solution containing 60 ppm Cl$^-$ in the presence and absence of inhibitors (TIPA – Zn^{2+} -TSC) are shown in figure-2 (a) and (b) (Nyquist Plots) and figure - 3a and 3b (Bode plots). The AC impedance parameter, namely, charge transfer resistance (R_t) and double layer capacitance (C_{dl}) derived from Nyquist plots are given in table 5.

It is observed that when the inhibitors (TIPA (100 ppm) - Zn^{2+} (50 ppm) –TSC (250 ppm) are added the charge transfer resistance (R_t) increases from 3149 cm^2 to 2398 cm^2. The C_{dl} value decreases from 5.07 x 10^{-7} F cm^{-2} to 6.66 x 10^{-10} F cm^{-2}. The impedance value [log (Z ohm^{-1})] increases from 3.3411 to 3.4620. These results lead to the conclusion that a protective film is formed on the metal surface.
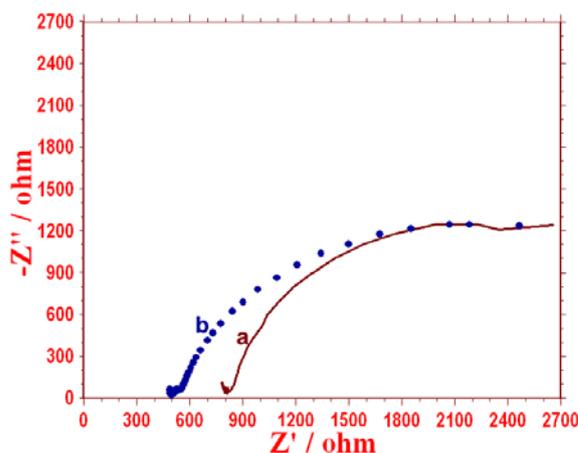
Figure 2. AC impedance spectra(Nyquist plot) of MS immersed in a) 60 ppm Cl$^-$ (Blank) b) TIPA (100 ppm) + Zn^{2+} (50 ppm) + TSC (250 ppm)
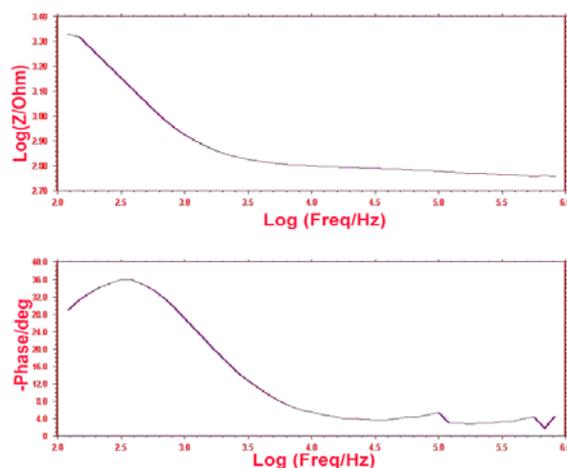
Figure 3a. AC impedance spectra of MS immersed in various test solutions (Bode Plot) a) 60 ppm Cl$^-$(Blank)
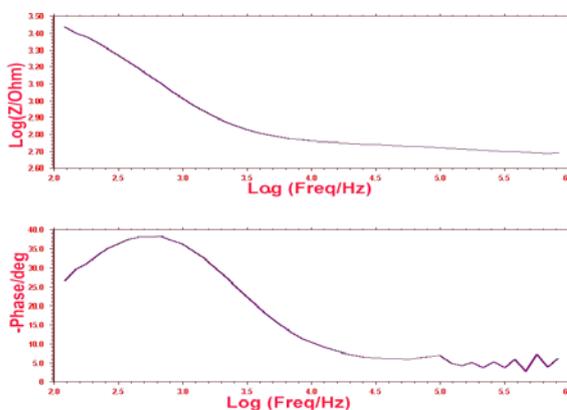
Figure 3b. AC impedance spectra of MS immersed in various test solutions (Bode Plot) a) TIPA (100 ppm) + Zn^{2+}(50 ppm) + TSC (250 ppm)

Table 5. Corrosion parameters of mild 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^{-1})]
A	3149	5.07×10^{-7}	3.3411
A+B	2398	6.66×10^{-10}	3.4620

A= Aqueous solution containing 60 ppm Cl^-; B= TIPA (100 ppm); Zn^{2+} (50 ppm); TSC (250 ppm)

FT-IR spectra

FT-IR spectra of TIPA+ Zn^{2+} is shown in figure 4a. The –NH stretching and –OH stretching frequency have overlapped and appear 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 Zn^{2+}, 250 ppm of TSC is shown in figure 4b. The –OH stretching frequency has shifted from 3350 cm^{-1} to 3427 cm^{-1}. The CN stretching frequency has shifted 1042 cm^{-1} to 1115 cm^{-1}. This suggest that TSC and TIPA coordinated with Fe^{2+} through their polar groups resulting in the formation of Fe^{2+}-TSC complex and Fe^{2+}-TIPA complex. The peak at 1416 cm^{-1} is due to Zn-O stretching.[15-16] The –OH stretching frequency appears at 3427 cm^{-1}. The C=O stretching frequency of TSC has shifted from 1599 cm^{-1} to 1562 cm^{-1}. This shift indicates that the carboxyl oxygen atom was coordinated to Fe^{2+} results in the formation of Fe^{2+}-TSC complex on the anodic sites of the metal surface. These results suggest the formation of $Zn(OH)_2$ on cathodic sites of the metal surface.
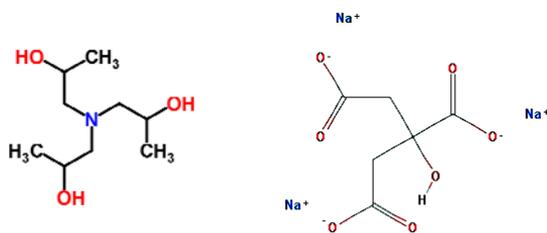
Scheme 1. Triisopropanolamine   **Scheme 2**. Trisodiumcitrate
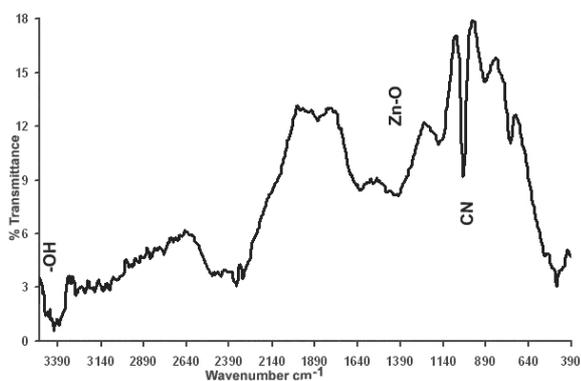
Figure 4a. Aqueous solution containing 60 ppm of Cl^- + 100 ppm of TIPA + 50 ppm of Zn^{2+}

Figure 4b. Aqueous solution containing 60ppm of Cl^- + 100 ppm of TIPA + 50 ppm of Zn^{2+} + 250 ppm of TSC

Conclusion

With these discussions, a mechanism may be proposed for the corrosion inhibition of carbon steel immersed in aqueous solution containing 60 ppm Cl^- by TIPA (100 ppm) – Zn^{2+}(50 ppm) - TSC (250 ppm) system. When the formulation consisting 60 ppm Cl^-, 100 ppm TIPA and 50 ppm of Zn^{2+}, there is formation of TIPA-Zn^{2+}, TSC-Zn^{2+} complex in solution. When mild steel immersed in this solution TIPA-Zn^{2+}, TSC-Zn^{2+} complex diffuses from the bulk of the solution towards the metal surface. TIPA-Zn^{2+}, TSC-Zn^{2+}complex are converted in to TIPA-Fe^{2+}, TSC-Fe^{2+}complex on the anodic sites of the metal surface with release of Zinc ion.

$$Zn^{2+}\text{-TIPA}, Zn^{2+}\text{-TSC} + Fe^{2+} \rightarrow Fe^{2+}\text{-TIPA}, Fe^{2+}\text{-TSC} + Zn^{2+}$$
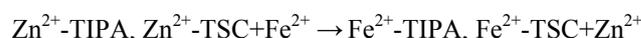
The released Zn^{2+} combines with OH$^-$ to form $Zn(OH)_2$ on the cathodic sites of the metal surface

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

Thus the protective film consists of TIPA-Fe^{2+}, TSC-Fe^{2+} complex and $Zn(OH)_2$. In aqueous solution the anodic reaction is the formation of Fe^{2+}. This anodic reaction is controlled by the formation of TIPA-TSC-Fe^{2+} complex on the anodic sites of the metal surface. The cathodic reaction is the formation of OH$^-$ which is controlled by the formation of $Zn(OH)_2$ on the cathodic sites of the metal surface

$$Fe \rightarrow Fe^{2+} + 2e^- \text{ (Anodic reaction)}$$

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \text{ (Cathodic reaction)}$$
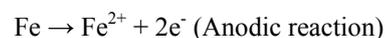
FTIR spectra reveal that protective film formed on the metal surface. This accounts for the synergistic effect of TIPA-Zn^{2+}-TSC system function as an anodic inhibitor.

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