



Trisodium Citrate As An Effective Corrosion Inhibitor For Carbon Steel In Chloride Environment

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Abstract— With the objective of developing a new environmental friendly inhibitor formulation for corrosion of carbon steel, Trisodium citrate (TSC) was chosen as inhibitor in 60 ppm Cl⁻ environment. Zn²⁺ was chosen as the synergist. The inhibition efficiency (IE) of various concentrations of a TSC-Zn²⁺ system in controlling corrosion of carbon steel immersed in 60ppm Cl⁻ environment was evaluated by a weight-loss study, electrochemical impedance spectroscopy and potentiodynamic polarization method. The result showed that when TSC alone was used the IE was less but in combination with Zn²⁺ as a synergist, IE increases. The most effective inhibitive effect was shown by 250ppm of TSC and 5ppm of Zn²⁺ as 98%. Synergism between Zn²⁺ and TSC has been calculated by synergism parameter. Polarisation study reveals that the inhibitor formulation was of mixed type. The protective film formed on the metal surface was confirmed by electrochemical impedance spectroscopy (EIS).The nature of the protective film has been characterized by FTIR, EDAX and FESEM.

Key words: Corrosion inhibitor, Trisodium Citrate, Carbon Steel, Polarization study, AC impedance spectra, FESEM, FTIR, EDAX

I. INTRODUCTION

Inhibitor is a chemical substance that, when added in a small concentration to an environment, effectively decreases the corrosion rate. Inhibitors are chemicals that interact with a metallic surface, or the environment to which the surface is exposed, giving the surface a certain level of protection. Inhibitors often work by adsorbing themselves on the metallic surface by forming a film. Inhibitors slow corrosion process by reducing the movement or diffusion of ions to the metallic surface increasing the electrical resistance to the metallic surface increasing the anodic or cathodic polarization behavior. Organic compounds containing one or more polar functions (with N, O, S atoms) have shown to be quite efficient to prevent corrosion. Hence, several carboxylic acids such as carboxymethyl cellulose, Thiomalic acid and Melonic acid have been used as inhibitors^[1-3]. It is suggested that the carboxylic acids compete successfully with Cl⁻ as a complexing agent for iron by forming strong

chemical bonds between carboxyl groups of carboxylic acids and Fe²⁺. Further the inhibition efficiency can be improved by the synergism effect of certain ions such as Zn²⁺^[4] Hence, in the present study, Trisodium citrate (TSC) along with Zn²⁺ as the synergist in various concentrations was chosen as the inhibitor for controlling corrosion of carbon steel in 60 ppm Cl⁻ environment. Corrosion inhibition was investigated using weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation methods (Tafel). Further confirmation of inhibitive action as formation of protective film on metal surface is obtained by FTIR, FESEM, and EDAX.

II. EXPERIMENTAL METHODS

A. Weight loss method

The weight losses are found by keeping exactly identical specimens for a constant time and temperature in the solution under study.IE is calculated by using the formula.

$$I.E=W_0-W_1\times 100/W_0$$

Where,

W₀=Weight loss in the absence of inhibitor

W₁=Weight loss in the presence of inhibitor

B. Electrochemical method

Electro chemical studies such as polarization and AC impedance were performed using Bio-logic SP300 with EC lab software and a three electrode cell assembly. Carbon steel was used as working electrode, platinum electrode as an auxiliary electrode and saturated calomel electrode (SCE) as the reference electrode. The working electrode (WE) freshly polished with exposed surface area 1cm² was immersed in test solution at open circuit potential until a steady state was reached. All potentials reported were measured versus SCE. Tafel curves were obtained at a scan rate of 1.0 mVs⁻¹. EIS measurements were performed under conditions in a frequency range from 10,000Hz to 0.01 Hz with amplitude of 10 mV AC signal. The experiments were carried out when the electrochemical system was in steady state in 60ppm Cl⁻

environment in the absence and presence of different concentrations of trisodium citrate.

The inhibition efficiency is calculated from the following relations.

$$IE \% = [(I_{\text{corr}}^* - I_{\text{corr}}) / I_{\text{corr}}^*] \times 100$$

Where,

I_{corr}^* and I_{corr} are current densities in the absence and presence of inhibitor respectively.

$$IE \% = (1/R_t^*) - (1/R_t) / 1/R_t^* \times 100$$

Where,

R_t^* and R_t are the charge transfer resistances in the absence and presence of inhibitor respectively.

C_{dl} value can be calculated by the following relation:

$$C_{dl} = 1/2\pi f_{\text{max}} R_{ct}$$

To obtain the value of double layer capacitance (C_{dl}), the values of frequency at which the maximum imaginary component of the impedance (f_{max}), is found and is used in the above equation with corresponding R_{ct} values.

C. Synergism Considerations

According to studies by Gomma^[5], the synergism parameter (S_I) can be calculated using the relationship given by Aramaki and Hackermann^[6].

$$S_I = \frac{1 - I_{1+2}}{1 - I_{1+2}}$$

Where,

$$I_{1+2} = (I_1 + I_2) - (I_1 I_2)$$

I_1 = Inhibition efficiency of TSC

I_2 = Inhibition efficiency of Zn^{2+}

I'_{1+2} = measured inhibition efficiency for TSC in Combination with Zn^{2+}

III. RESULTS AND DISCUSSION

Analysis of the results of the weight-loss method

The inhibition efficiencies (IE) and corrosion rates of various concentrations of TSC in controlling corrosion of carbon steel immersed in 60ppm of chloride environment for a period of three days in the presence and absence of Zn^{2+} by weight loss method are given in Table 1.

Table 1: Inhibition efficiencies (IE %), Corrosion Rates (CR)* in mpy and synergism parameter (S_I) (given in parentheses) obtained from TSC- Zn^{2+} system, when carbon steel was immersed in 60 ppm Cl^- environment for three days.

TSC (ppm)	IE %, CR*, S_I (given in parentheses)			
	Zn^{2+} (ppm)			
	0	5	10	25
Blank	- 3.9623*	5 3.7642*	8 3.6453*	22 3.0906*

50	13 3.4472*	50 1.9812* (0.94)	25 2.6415* (3.5)	40 2.3774* (6.5)
100	25 2.6415*	63 1.4661* (1.53)	38 2.4566* (4.5)	55 1.7830* (9.3)
150	50 1.9812*	75 0.9906* (2.62)	50 1.9812* (7.0)	64 1.4264* (16.3)
200	63 1.4661*	88 0.4755* (2.85)	75 0.9906* (5.9)	85 0.5943* (15.9)
250	75 0.9906*	98 0.0792* (3.05)	98 0.0792* (6.8)	98 0.0792* (16.0)

TSC alone has some IE whereas Zn^{2+} ions alone was found to be corrosive. When TSC was combined with Zn^{2+} ions it was found that the IE increased with increase in concentration of TSC. For example 250 ppm of TSC had only 75% IE and 5 ppm of Zn^{2+} ions had only 50 % IE. Interestingly their combinations showed 98 per cent IE. This suggests that TSC and Zn exhibit synergistic behaviour. The anodic reactions are retarded by the formation of Fe^{2+} -TSC complex. In the presence of Zn^{2+} ion the cathodic reaction was also retarded by the formation of $Zn(OH)_2$ on the cathodic sites of the metal surface. This was confirmed by the FTIR study which revealed the presence of Fe^{2+} -TSC complex and $Zn(OH)_2$ on the metal surface^[7].

The calculated S_I values are listed in parentheses in Table 1 for different concentrations of inhibitors^[4]. S_I Approaches 1 where no interaction between the inhibitor compounds exists. When $S_I > 1$, which points to synergistic effects. In the case of $S_I < 1$, the negative interaction of inhibitors prevails (i.e corrosion rate increases). From Table 1, it can be seen that most values of S_I are greater than unity, suggesting that the phenomenon of synergism exists between TSC and Zn^{2+} . Thus the enhancement of the inhibition efficiency caused by the addition of Zn^{2+} ions to TSC is only due to synergistic effect.

Analysis of the results of potentiodynamic polarization study:

Polarization study has been used to study the formation of protective film on the metal surface. The corrosion parameters namely corrosion potential (E_{corr}), Tafel slopes b_a and b_c , and corrosion current (I_{corr}) of mild steel immersed in various test solutions obtained by polarization study are given in Table 2.

Table 2: Corrosion parameters of carbon steel immersed in 60 ppm Cl^- environment in the presence and absence of inhibitors obtained from potentiodynamic polarization study.

Inhibitor system	E_{corr} (mv vs SCE)	I_{corr} (μA Cm-2)	β_a mv dec-	β_c mv dec-	I.E %
Blank	-446	6.01	72.7	13.7	-
Zn^{2+} (5 ppm)	-492	1.39	48.1	11.0	42.5

TSC (250 ppm) + Zn ²⁺ (5 ppm)	-364	1.08	70.5	8.0	33.0
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The potentiodynamic polarization curves of carbon steel immersed in 60 ppm Cl⁻ environment in the absence and presence of inhibitors are shown in Figure 1. It is observed that when carbon steel immersed in 60 ppm Cl⁻ environment, the E_{corr} value is -446 mV vs SCE and the I_{corr} value is 6.01 μA cm⁻². When 250 ppm of TSC and 5 ppm of Zn²⁺ are added to the above environment, the corrosion potential E_{corr} value is observed to be -364 mV vs SCE which is shifted to the anodic side. However, the values of Tafel slopes are almost equal. Hence TSC- Zn²⁺ system functions as a mixed inhibitor [8, 9]. These observations suggest the formation of a protective film on the metal surface.

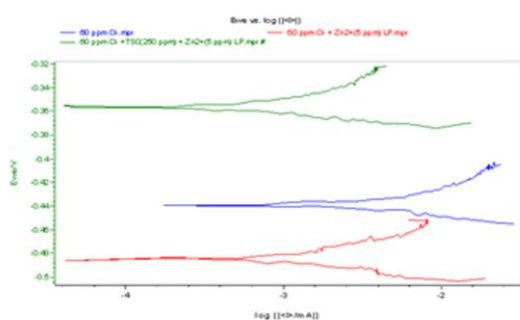


Figure 1. Typical polarization curves for corrosion of carbon steel in 60 ppm Cl⁻ in the absence and presence of 250 ppm of TSC and 5 ppm of Zn²⁺

Analysis of AC impedance spectra

AC impedance spectra of carbon steel immersed in 60 ppm Cl⁻ environment in the absence and presence of inhibitors are shown in Figure 2 (Nyquist plots). The corrosion parameters namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) derived from Nyquist plots are given in Table 3. It is observed that when carbon steel immersed in 60 ppm Cl⁻ environment R_t value is 1675 Ω cm². The C_{dl} value is 3.00 × 10⁻³ F cm². When inhibitors (250 ppm of TSC + 5 ppm of Zn²⁺) are added the R_t values increases from 1675 to 17041 Ω cm². The C_{dl} value decreases from 3.00 × 10⁻³ to 93.24 × 10⁻⁶ F cm². This decrease in C_{dl} results from a decrease in local dielectric constant and/or an increase in the thickness of the double layer, suggested that inhibitor molecules inhibit the iron corrosion by adsorption at the metal/ Cl⁻ environment interface [10]. These observations suggest that a protective film is formed on the metal surface.

Table 3. Corrosion parameters of carbon steel immersed in 60 ppm Cl⁻ environment in the presence and absence of inhibitor obtained from electrochemical impedance spectroscopy.

Inhibitor system	R _t (Ω cm ²)	C _{dl} (F cm ⁻²)	IE%
Blank	1675	3.00 × 10 ⁻³	-
Zn ²⁺ (5 ppm)	3407	0.2617 × 10 ⁻³	50.8
TSC (250 ppm) + Zn ²⁺ (5 ppm)	17041	93.24 × 10 ⁻⁶	90.2

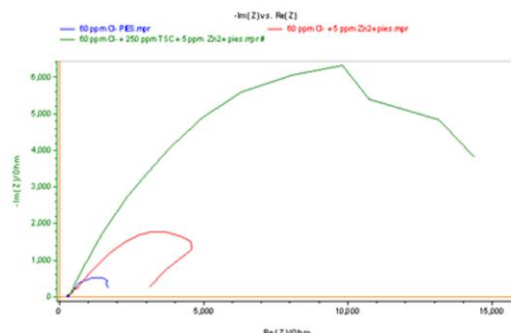


Figure 2. Nyquist plots for corrosion of carbon steel in 60 ppm Cl⁻ in the absence and presence of 250 ppm of TSC and 5 ppm of Zn²⁺

Analysis of FTIR spectra

The FTIR spectra have been used to analyze the film formed on the metal surface.

FTIR spectrum of pure TSC is shown in Figure 3. The C=O stretching frequency occurs at 1579 cm⁻¹. The FTIR spectrum of the film scratched from the surface of the metal immersed in 60 ppm chloride environment, 250 ppm of TSC and 5 ppm of Zn²⁺ is given in Figure 4. It is observed from the spectrum that the C=O stretching frequency of TSC in the free state has shifted from 1579 cm⁻¹ to 1583 cm⁻¹. This shift indicates that the carbonyl oxygen atom was coordinated to Fe²⁺ resulting in the formation of Fe²⁺-TSC complex on the anodic sites of the metal surface [11-13]. The band at 1066 cm⁻¹ was appeared due to the presence of Zn(OH)₂ [14].

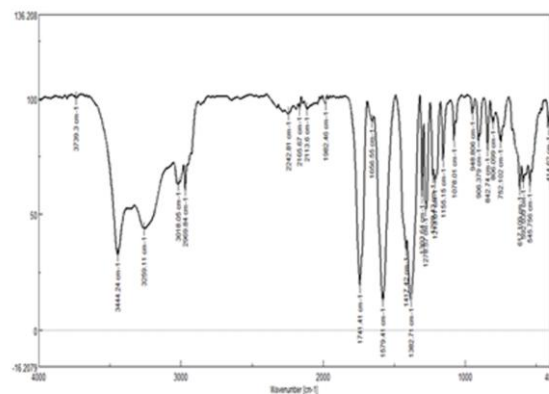


Figure 3. FTIR spectra of pure Trisodium Citrate

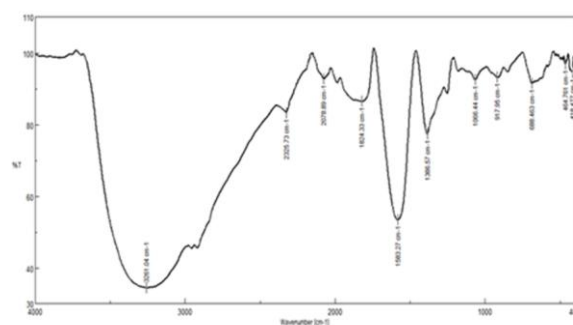


Figure 4. FTIR spectra of the metal immersed in chloride environment, TSC (250 ppm) and Zn²⁺ (5 ppm)

Analysis of Energy Dispersive X-ray Spectrometry (EDAX)

The EDAX spectra were used to determine the element present on the metal surface before and after exposure to the inhibitor solution. The objective of this section was to confirm the results obtained from chemical and electrochemical measurements that a protective surface film of inhibitor is formed on the metal surface.

EDAX spectrum of polished carbon steel is shown in Figure 5. EDAX spectrum of carbon steel immersed in aqueous solution containing 60 ppm Cl⁻ is shown in Figure 6. They show the characteristic peaks of some of the elements constituting the carbon steel sample. The EDAX spectrum of carbon steel immersed in aqueous solution containing 60ppmCl⁻, 250 ppm (TSC) and 5ppm Zn²⁺ is shown in Figure 7. In addition, the intensity of Fe signals is reduced and the intensity of O signal is increased as observed from the table 4. The enhancement of O signal is due to the presence of inhibitor. These data show that the metal surface is covered by the Fe, O, C, and Cl atoms.

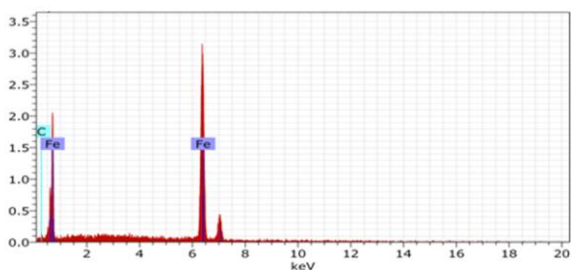


Figure 5. EDAX spectra for polished carbon steel

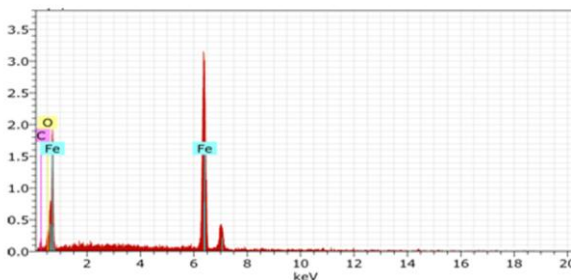


Figure 6. EDAX spectra for carbon steel immersed in 60 ppm Cl⁻ environment.

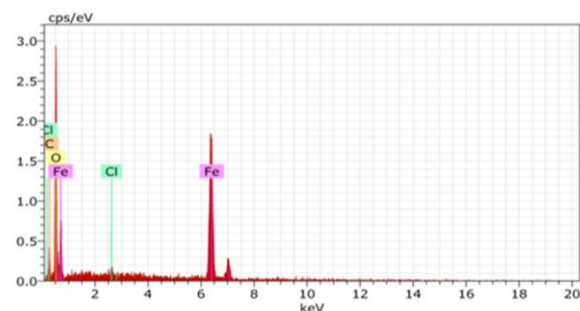


Figure 7. EDAX spectra of the metal immersed in 60 ppm chloride environment, TSC (250 ppm) and Zn²⁺ (5ppm)

Table 4. The composition of elements present in carbon steel in various environments

Element	Atomic percent	Metal under study
Fe	81.11	Polished carbon steel
C	18.89	
Fe	64.18	Carbon steel immersed in 60 ppm Cl ⁻
C	23.78	
O	12.04	
Fe	19.43	Carbon steel immersed in 60 ppm Cl ⁻ , TSC (250 ppm) and Zn ²⁺ (5ppm)
O	56.44	
C	23.68	
Cl	0.45	

SEM analysis of metal surface

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 carbon steel, the SEM micrographs of the surface are examined.

The SEM micrograph of polished carbon steel surface (control) in Figure 8(i) shows the smooth surface of the metal. This shows the absence of any corrosion products or inhibitors complex formed on the metal surface. The SEM micrographs of carbon steel surface immersed in 60 ppm Cl⁻ environment is shown in Figure 8(ii) shows the roughness of the metal surface which indicates the corrosion of carbon steel in Chloride environment. Figure 8(iii) shows the SEM micrograph of the metal surface immersed in chloride environment containing 250 ppm of TSC, 5ppm of Zn²⁺ and it establishes the protective layer formation which shows the evidence for inhibition of carbon steel dissolution.

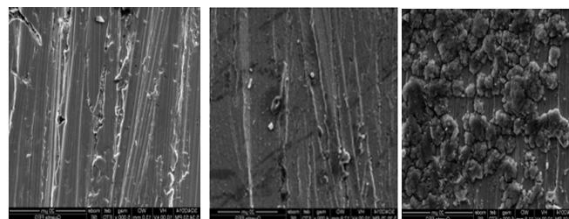


Figure 8. SEM micrographs

(i)Mild steel Magnification-X 5000

(ii)Mild steel immersed in chloride environment;Magnification-X 5000

(iii)Mild steel immersed in chloride environment containing TSC(250 ppm)+ Zn²⁺ (5 ppm);Magnification-X5000

Mechanism of corrosion inhibition by the TSC-Zn²⁺ system

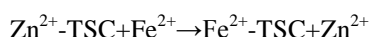
The results of the weight loss study shows that the formulation consisting of 250 ppm of TSC and 5 ppm of Zn²⁺ has 98% IE in controlling corrosion of mild steel in

chloride environment .A synergistic effect exists between Zn^{2+} and TSC .Polarization study reveals that the formulation functions as anodic inhibitor controlling the anodic reaction predominantly and to some extent controls the cathodic reaction.AC impedance spectra reveals that a protective film is formed on the metal surface. FTIR spectra study reveal that the protective film consists of Fe^{2+} -TSC complex and $Zn(OH)_2$.

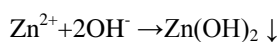
When the solution containing 60 ppm Cl^- , 5ppm of Zn^{2+} and 250 ppm TSC was prepared, there was formation of Zn^{2+} -TSC complex in solution

When carbon steel was immersed in this solution,the Zn^{2+} -TSC complex diffused from the bulk of the solution towards metal surface.

On the metal surface, Zn^{2+} - TSC complex was converted into Fe^{2+} -TSC complex on the anodic sites. Zn^{2+} was released.



The released Zn^{2+} combines with OH^- and forms $Zn(OH)_2$ on the cathodic sites.



Thus the protective film consisted of Fe^{2+} -TSC complex and $Zn(OH)_2$.

IV. CONCLUSION

The results of the weight loss study shows that the formulation consisting of 250 ppm of TSC and 5 ppm of Zn^{2+} has 98% IE in controlling corrosion of mild steel in chloride environment .A synergistic effect exists between Zn^{2+} and TSC. Polarization study reveals that the formulation functions as anodic inhibitor controlling the anodic reaction predominantly and to some extent controls the cathodic reaction.AC impedance spectra reveals that a protective film is formed on the metal surface .FTIR reveals that the protective film consists of Fe^{2+} -TSC complex and $Zn(OH)_2$.The SEM, EDAX micrographs confirm the formation of protective layer on the metal surface.

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