

Effect of Na_3PO_4 on the corrosion inhibition efficiency of EDTA – Zn^{2+} system for carbon steel in aqueous solution

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The synergistic effect of sodium salt of ethylene diamine tetra acetic acid (EDTA) and Zn^{2+} in controlling corrosion of carbon steel in an aqueous environment containing 60 ppm Cl^- was evaluated by weight loss and electro chemical methods. A formulation consisting of 50 ppm EDTA and 50 ppm Zn^{2+} was observed to achieve 73% inhibition efficiency. Influence of Na_3PO_4 on EDTA - Zn^{2+} was studied and IE was found to increase from 73 to 98%. A suitable mechanism of corrosion inhibition has been proposed which is based on the results obtained from weight loss method, polarization study, AC impedance spectra and FTIR spectra. The protective film consisted of Fe^{2+} - EDTA, Fe^{2+} - Na_3PO_4 complexes and $\text{Zn}(\text{OH})_2$.

Keywords: Carbon steel, Corrosion inhibition, EDTA, Na_3PO_4 , Synergistic effect

Inhibition of metal corrosion by organic compounds is a result of adsorption of organic molecules or ions at the metal surface forming a protective layer. This layer reduces or prevents corrosion of the metal. The extent of adsorption depends on the nature of the metal, the metal surface condition, the mode of absorption, the chemical structure of the inhibitor, and the type of corrosive media¹. Hetero atoms in the structure of inhibitor molecules such as oxygen, nitrogen, phosphorous, sulphur and the presence of aromatic rings of triple bond enhance the adsorption process. It has been reported that the inhibition efficiency increases in the order. $\text{O} < \text{N} < \text{S} < \text{P}^{2-5}$.

Numerous organic compounds serve effectively as corrosion inhibitors in aqueous media. These include the triple bonded hydrocarbons; acetylenic alcohols; sulphonides; sulphides and mercaptans; aliphatic, aromatic or heterocyclic compounds containing nitrogen; and many other classes of simple organic compounds or of condensation products formed by the reaction between two different species such as aldehydes and amines. Inhibitors that change cathodic or anodic processes kinetically also are important additives in the technological processes of metal deposition⁶⁻⁸.

Among these inhibitors ethylene diamine tetra acetic acid (EDTA) has been used due to its ability to form metal complexes, stabilizing property,

sequestering property and inhibiting property^{9,10}. Joshi *et al.*¹¹ have made a comparison between the passivation behaviour of carbon steel in the presence of EDTA, Ni(II)-EDTA and LiOH dosed deoxygenated aqueous media at 473K. Capobianco *et al.*¹² have investigated the mechanism of corrosion inhibition of carbon steel by EDTA - hydroxylamine sulphate. Gallic acid as corrosion inhibitor of carbon steel in chemical decontamination formulation can be used. It was observed that gallic acid along with EDTA provided 31% corrosion inhibition to carbon steel¹³.

For several years, stabilized phosphate programmes have become industrial standards for the treatment of industrial open evaporative cooling systems¹⁴. The most important phosphates used in cooling water systems are ortho- phosphates, pyro-phosphates, poly phosphates, and tri-polyphosphates. The mechanism of corrosion inhibition by different phosphates has been discussed¹⁵. Saha and Kurmaih¹⁶ have investigated the mechanism of corrosion inhibition by phosphate-based corrosion inhibitors for cooling system. Akolvin *et al.*¹⁷ have studied the inhibitor of corrosion of carbon steel by potassium phosphate in bacterial culture acid.

The present work is undertaken (i) To evaluate the inhibition efficiency of EDTA in controlling corrosion of carbon steel in neutral aqueous

environment containing 60 ppm Cl^- (ii) To study the influence of duration of immersion and pH on the inhibition efficiency of EDTA-Zn^{2+} and $\text{Na}_3\text{PO}_4\text{-Zn}^{2+}$ systems (iii) To analyse the protective film by FTIR and (iv) To make use of polarisation study and AC impedance spectra to know the mechanistic aspects of corrosion inhibition.

Experimental Procedure

Preparation of specimens

The carbon steel used in this study had the following composition: S, 0.03; P, 0.04; Mn, 0.4 C, 0.15; and Fe, remainder. Carbon steel specimens of the dimensions $1 \times 4 \times 0.2 \text{ cm}^3$ polished to mirror finish and degreased with trichloroethylene, were used for the weight-loss and surface examination studies.

Weight loss method

Carbon steel specimens, in triplicate, were immersed in 100 mL of solution containing 60 ppm Cl^- and various concentrations of inhibitor in the absence and presence of Zn^{2+} , for three days. The weights of the specimens before and after immersion were determined using a Mettler balance, AE-240. The corrosion products were cleaned with Clarke's solution¹⁸. The percent IE was calculated using the relation, $\text{IE} = (W_1 - W_2)/W_2 \times 100$, where W_1 and W_2 are weight losses of carbon steel in uninhibited and inhibited chloride solutions.

Surface examination study

The carbon steel specimens were immersed in various test solutions for three days. After three days, the specimens were taken out, rinsed with water thoroughly and dried. The nature of the film formed on the surface of the metal specimens was analysed by various surface analysis techniques.

Fourier transform infrared spectra

FTIR spectra (KBr) were recorded using a Perkin - Elmer - 1600 FTIR spectrophotometer.

Potentiostatic polarization study

Potentiostatic polarization study and AC impedance were carried out using CHI electrochemical impedance analyzer, 660A model. A three - electrode cell assembly was used. Carbon steel was used as the working electrode. A saturated calomel electrode (SCE) was used as the reference electrode and platinum was used as the counter electrode. The results such as Tafel slopes, I_{Corr} and E_{Corr} values were calculated.

AC impedance measurement

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.

Results and Discussion

Weight loss study

The inhibition efficiencies (IEs) of EDTA in controlling corrosion of carbon steel immersed in aqueous solution containing 60 ppm of Cl^- for three days in the presence and absence of Zn^{2+} obtained by weight loss methods are given in Table 1. EDTA alone has some IE and Zn^{2+} alone is not a good inhibitor. IE decreases with increase in the concentration of EDTA and Zn^{2+} . A synergistic effect between EDTA and Zn^{2+} exists. For example 50 ppm of Zn^{2+} has 23% IE and 50 ppm EDTA has 60% IE. However the formulation consisting of 50 ppm EDTA and 50 ppm Zn^{2+} shows 73% IE.

Influence of Na_3PO_4 on the IE of EDTA - Zn^{2+} system

The IEs of various concentrations of Na_3PO_4 - Zn^{2+} system are given in Table 2. The influence of Na_3PO_4

Table 1 — Corrosion inhibition efficiencies (%) offered by EDTA- Zn^{2+} system to mild steel immersed in 60 ppm Cl^- medium for three days

EDTA (ppm)	Inhibition efficiency Zn^{2+} (ppm)				
	0	5	10	25	50
0	0	7	10	13	23
50	60	50	62	64	73
100	48	43	45	48	71
150	45	38	38	43	64
200	24	29	31	36	62
250	12	26	29	21	40

Table 2 — Corrosion inhibition efficiencies (%) offered by Na_3PO_4 - Zn^{2+} system to mild steel immersed in 60 ppm Cl^- medium for three days

Na_3PO_4 (ppm)	Inhibition efficiency Zn^{2+} (ppm)	
	0	5
0	0	23
50	19	67
100	18	50
150	17	47
200	21	43
250	24	40

on the inhibition efficiency of EDTA (50 ppm) - Zn²⁺ (50 ppm) system is given in Table 3. It is derived from these results that 50 ppm of Na₃PO₄ in combination with EDTA - Zn²⁺ has increased IE from 73 to 98%. However a decrease in corrosion inhibition efficiency of EDTA - Zn²⁺ system is noticed when the Na₃PO₄ concentration is increased from 50 ppm to 250 ppm.

Influence of immersion period on the IE of EDTA- Na₃PO₄- Zn²⁺ system

The influence of immersion period on the IE of Zn²⁺ (50 ppm)- EDTA (50 ppm)- Na₃PO₄ (50 ppm) is given in Table 4. It is found that as the immersion period increases, IE decreases. This is due to the fact that as the period of immersion increases, the protective film formed on the metal surface gets ruptured by the aggressive chloride ion present in the environment. Further there is a competition between the formation of FeCl₂ (and also FeCl₃) and formation of Fe²⁺ - EDTA and Fe²⁺-Na₃PO₄ complexes. It seems that as the immersion period increases the formation of FeCl₂ is more favoured than the formation of Fe²⁺ - EDTA and Fe²⁺ - Na₃PO₄ complexes at the anodic sites of the metal. Hence a decrease in inhibition efficiency is noticed as the period of immersion increases. Similar observations have been made by Selvaraj *et al.*¹⁹ while studying the corrosion inhibition of carbon steel in the presence of polyvinyl pyrrolidone and also by Rajendran *et al.*²⁰ while studying corrosion inhibition by sodium dodecyl sulphate.

Influence of pH on inhibition efficiency

The influence of pH on IE of EDTA (50 ppm), Na₃PO₄ (50 ppm) and Zn²⁺ (50 ppm) system is given in Table 5. It is found that at pH 7 the IE is 98%. When acid is added (pH 5), IE decreases. The protective film is broken by H⁺ ions of the acid. When NaOH is added (pH 10), IE decreases. Zn²⁺ is not able to transport EDTA and Na₃PO₄ towards the metal surface, as Zn²⁺ is precipitated as Zn(OH)₂ in the bulk of the solution. The same thing happens at pH 12 also.

Potentiostatic polarization study for EDTA- Zn²⁺ and Na₃PO₄- Zn²⁺ systems

The corrosion parameters of carbon steel immersed in various test solutions obtained by polarization study are given in Table 6. The polarization curves are shown in Fig. 1. When carbon steel is immersed in water containing 60 ppm of Cl⁻ the corrosion potential is -553.57 mV versus saturated calomel electrode (SCE). The formulation consisting of 50 ppm of EDTA, 50 ppm of Na₃PO₄ and 50 ppm of Zn²⁺ shifts the corrosion potential to -500 mV versus SCE, since more Na₃PO₄ is transported to the anodic sites in the presence of Zn²⁺. The corrosion current for aqueous solution containing 60 ppm of Cl⁻ is 2.194 x 10⁻⁵ A/cm². The corrosion current for formulation consisting of 60 ppm of Cl⁻, EDTA (50 ppm), Zn²⁺ (50 ppm) and Na₃PO₄ (50 ppm) has decreased to 1.905 x 10⁻⁵ A/cm². This is due to the formation of a protective film formed on the metal surface.

AC impedance spectra

The AC impedance spectra of carbon steel immersed in various solutions were recorded (Fig. 2). The AC impedance parameters, namely charge transfer resistance (*R_t*) and double layer capacitance (*C_{dl}*) are given in Table 7.

An aqueous solution containing 60 ppm of Cl⁻ has *R_t* value of 441.71 Ωcm² and *C_{dl}* value of 1.153 x 10⁻⁸ μFcm⁻². In the presence of Na₃PO₄, EDTA and Zn²⁺, *R_t* value increases from 441.71 to 470.48 Ωcm². The *C_{dl}* decreases from 1.153 x 10⁻⁸ to 1.083 x 10⁻⁸ μFcm⁻². This suggests that a protective film is formed on the

Table 3 — Corrosion inhibition efficiencies (%) offered by EDTA - Na₃PO₄ - Zn²⁺ system to mild steel immersed in 60 ppm Cl⁻ medium for three days

EDTA (ppm)	Zn ²⁺ (ppm)	Na ₃ PO ₄ (ppm)	CR (mdd)	IE (%)
0	0	0	38.18	-
50	50	0	9.16	73
50	50	50	0.76	98
50	50	100	7.25	81
50	50	150	11.07	71
50	50	200	11.83	69
50	50	250	12.59	67

Table 4 — Influence of immersion period on the inhibition efficiency of the EDTA - Na₃PO₄- Zn²⁺ system

Immersion period (days)	3	5	7	9
System : Aqueous medium containing 60 ppm Cl ⁻ CR (mdd)	38.18	25.75	21.63	21.81
System : Aqueous medium containing 60 ppm Cl ⁻ EDTA (50 ppm) + Zn ²⁺ (50 ppm) CR(mdd) +Na ₃ PO ₄ (50 ppm)	0.76	22.90	24.43	27.48
IE (%)	98	40	36	28

surface of the metal. This accounts for the very high IE of Na_3PO_4 - Zn^{2+} and EDTA - Zn^{2+} systems.

FTIR spectra

FTIR spectrum of pure EDTA is shown in Fig. 3a. The C-N and C=O stretching frequency of carboxyl group appear at 1192 and 1624 cm^{-1} respectively. In the spectrum of the film (Fig. 3b) the C-N stretching frequency has shifted from 1192 to 1112 cm^{-1} . The C=O stretching frequency has shifted from 1624 to 1634 cm^{-1} . This indicates that EDTA has

coordinated to the Fe^{2+} on the anodic sites of the metal surface^{21,22}. The N atom and O atom have coordinated with Fe^{2+} . The peak at 1327 cm^{-1} is due to $\text{Zn}(\text{OH})_2$ formed on the cathodic sites²³⁻²⁶. Thus FTIR spectra lead to the conclusion that the protective film consists of Fe^{2+} -EDTA and $\text{Zn}(\text{OH})_2$.

FTIR spectrum of pure Na_3PO_4 is shown in Fig. 4a. The P-O stretching frequency appears at 1119 cm^{-1} . The FTIR spectrum of the film formed on the surface of the metal after immersion in the solution containing 50 ppm of Zn^{2+} , 50 ppm of EDTA and 50 ppm of Na_3PO_4 is shown in Fig. 4b. It is found that the P-O stretching frequency of Na_3PO_4 has decreased

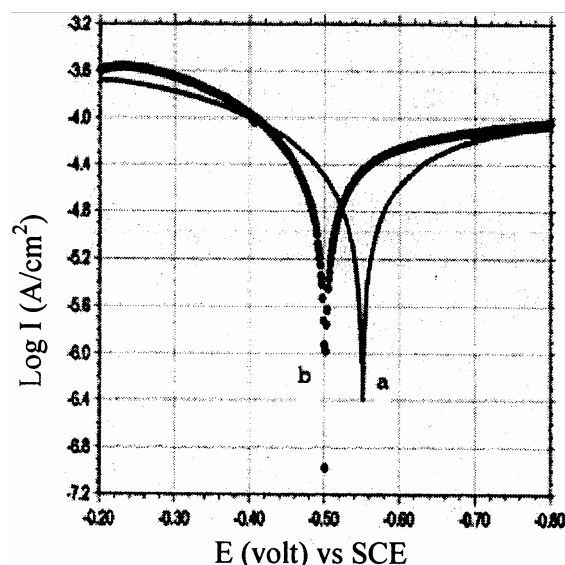


Fig. 1—Polarisation curves of carbon steel immersed in various test solutions; (a) 60 ppm Cl^- , (b) 60 ppm Cl^- + EDTA (50 ppm) + Zn^{2+} (50 ppm) + Na_3PO_4 (50 ppm)

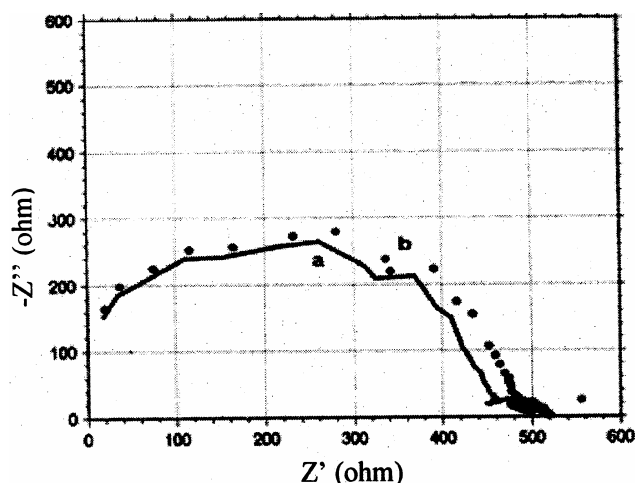


Fig. 2 — AC impedance spectra of carbon steel immersed in various test solutions; (a) 60 ppm Cl^- , (b) 60 ppm Cl^- + EDTA (50 ppm) + Zn^{2+} (50 ppm) + Na_3PO_4 (50 ppm)

Table 5 — Influence of various pH on the inhibition efficiency of the EDTA (50 ppm) - Na_3PO_4

pH	(50 ppm) - Zn^{2+} (50 ppm) system				
	3	5	7	10	12
System : Aqueous solution containing 60 ppm Cl^- CR (mdd)	35.45	19.09	38.18	18.18	15.45
System : Aqueous solution containing 60 ppm Cl^- + EDTA (50ppm) + Zn^{2+} (50 ppm) + Na_3PO_4 (50 ppm)					
CR (mdd)	6.74	2.29	0.76	0.73	2.63
IE (%)	81	88	98	96	83

Table 6 — Corrosion parameters of carbon steel immersed in aqueous solution containing 60 ppm Cl^- in the absence and presence of inhibitor obtained by polarization method

System	E_{corr} mV vs SCE	b_a (mV)	b_c (mV)	I_{corr} (A/cm^2)
Aqueous solution containing 60 ppm Cl^-	-553.57	203.57	296.42	2.194×10^{-5}
Aqueous solution containing 60 ppm Cl^- + EDTA (50 ppm) + Na_3PO_4 (50 ppm) + Zn^{2+} (50 ppm)	- 500	96.42	175	1.905×10^{-5}

Table 7 — Impedance parameters of carbon steel immersed in aqueous solution containing 60 ppm Cl⁻ in the presence and absence of inhibitor by AC impedance method

System	R_t (Ωcm^2)	C_{dl} ($\mu\text{F}/\text{cm}^2$)
Aqueous solution containing 60 ppm Cl ⁻	441.71	1.153×10^{-8}
Aqueous solution containing 60 ppm Cl ⁻ + EDTA (50 ppm) + Na ₃ PO ₄ (50 ppm) + Zn ²⁺ (50 ppm)	470.48	1.083×10^{-8}

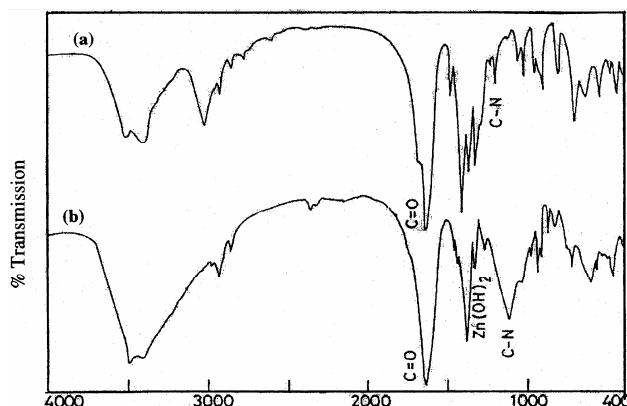


Fig. 3 — FTIR spectra: (a) Pure EDTA, (b) Film formed on surface of metal after immersion in an aqueous solution containing 60 ppm of Cl⁻ + EDTA (50 ppm) + Zn²⁺ (50 ppm)

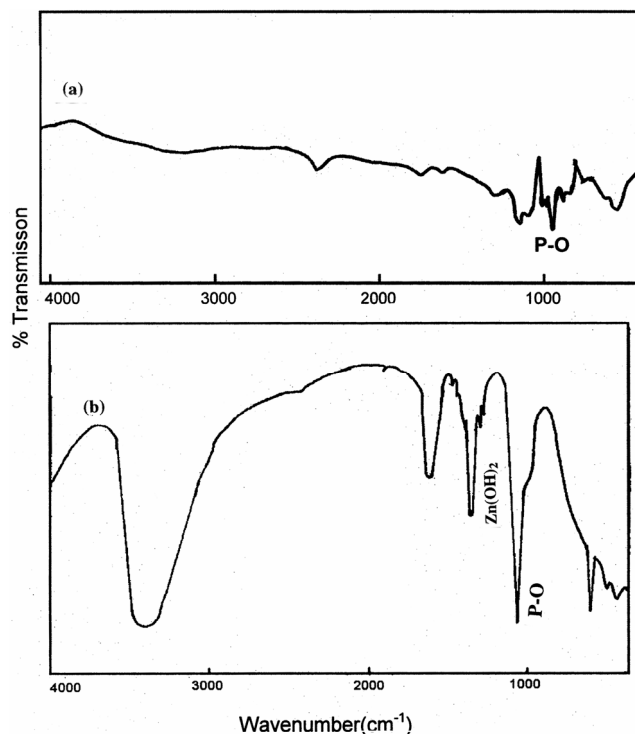


Fig. 4 — FTIR spectra: (a) Pure Na₃PO₄, (b) Film formed on surface of metal after immersion in an aqueous solution containing 60 ppm Cl⁻ + EDTA (50 ppm) + Zn²⁺ (50 ppm) + Na₃PO₄ (50 ppm)

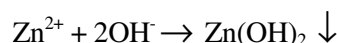
from 1119 to 991 cm⁻¹. This suggests the formation of Fe²⁺-Na₃PO₄ complex on the anodic sites of the metal surface. Similarly, the C=O stretching frequency has decreased from 1624 to 1605 cm⁻¹. This suggests the formation of Fe²⁺ - EDTA complex on the anodic sites of the metal surface. The peak at 1342 cm⁻¹ is due to Zn(OH)₂ formed on the cathodic sites²³⁻²⁶.

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⁻, 50 ppm of EDTA, 50 ppm of Zn²⁺ and 50 ppm of Na₃PO₄ is prepared, there is formation of Zn²⁺-EDTA and Zn²⁺-Na₃PO₄ complexes in solution.
- (ii) When carbon steel is immersed in the solution, the Zn²⁺-EDTA and Zn²⁺-Na₃PO₄ complexes diffuse from the bulk of the solution towards the metal surface.
- (iii) On the metal surface, Zn²⁺-EDTA and Zn²⁺-Na₃PO₄ complexes are converted into Fe²⁺-EDTA and Fe²⁺-Na₃PO₄ complexes on the anodic sites. Zn²⁺ is released.
- (iv) $\text{Zn}^{2+} - \text{EDTA} + \text{Fe}^{2+} \rightarrow \text{Fe}^{2+} - \text{EDTA} + \text{Zn}^{2+}$
- (v) $\text{Zn}^{2+} - \text{Na}_3\text{PO}_4 + \text{Fe}^{2+} \rightarrow \text{Fe}^{2+} - \text{Na}_3\text{PO}_4 + \text{Zn}^{2+}$

The released Zn²⁺ combines with OH⁻ to form Zn(OH)₂ on the cathodic sites.



Conclusions

The present study leads to the following conclusions

- (i) The formulation consisting of 50 ppm of EDTA, 50 ppm of Na₃PO₄ and 50 ppm of Zn²⁺ has 98% IE.
- (ii) Polarization study reveals that EDTA-Zn²⁺ and Na₃PO₄ -Zn²⁺ systems 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 Fe²⁺-EDTA and Fe²⁺-Na₃PO₄ complexes and Zn(OH)₂.

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