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Ethylenediaminetetraacetic Acid-Zn^{2+} System as Corrosion Inhibitor for Carbon Steel in Sea Water

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The inhibition efficiency of ethylenediaminetetraacetic acid (EDTA) in controlling corrosion of carbon steel in sea water in absence and presence of Zn^{2+} has been evaluated by weight loss method. The formulation consisting of 250 ppm EDTA and 50 ppm Zn^{2+} has 96 % inhibition efficiency. It is found that the inhibition efficiency of EDTA increases by the addition of Zn^{2+} ion. A synergistic effect exists between EDTA and Zn^{2+}. Polarization study reveals that EDTA-Zn^{2+} system functions as mixed inhibitor and the formulation controls the cathodic reaction predominantly. FTIR spectra reveal that the protective film consists of Fe^{2+}-EDTA complex and $Zn(OH)_2$. The surface morphology of the protective film on the metal surface was characterized by SEM study.

Key Words: Corrosion inhibition, EDTA, Carbon steel, Synergistic effect, Sea water.

INTRODUCTION

Corrosion inhibition can be done by the application of inhibitors. It is noted that the effect of corrosion inhibitors always causes a change in the state of surface being protected due to adsorption or formation of hardly soluble compounds with metal cations. Hetero atoms in the structure of inhibitor molecules such as oxygen, nitrogen, phosphorus, 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 O < N < S < P[1-4]. Numerous organic compounds serve effectively as corrosion inhibitors in sea water[5-10]. Among these inhibitors ethylenediaminetetra-acetic acid (EDTA) has been used due to its ability to form metal complexes, stabilizing property, sequestering property and inhibiting property[11-13] (Fig. 1). Ahmed and Musa[14] have investigated the corrosion inhibition of mild steel in presence of EDTA. Inhibition by EDTA and its di- and *tetra*-sodium salts, as well as its metal chelates has been reported[15-19]. The corrosion inhibition mechanism of carbon steel by EDTA has been reported[20]. The corrosion inhibition of carbon steel in an aqueous solution in presence of EDTA has been studied by Umamathi *et al.*[21]. Qu *et al.*[22] have investigated the effect of EDTA on the corrosion inhibition of steel in the presence of benzotriazole in acid media. The protective film formed on the mild steel in neutral aqueous solution has also been reported[23].

The aim of the present study is to investigate synergistic corrosion inhibition for the EDTA and Zn^{2+} combination to carbon steel in sea water collected from Bay of Bengal, Marina beach, Chennai. The corrosion inhibition efficiency was calculated using weight loss method and polarization study. The protective film formed on the metal surface characterized using surface morphological studies such as Fourier transform infrared spectra and scanning electron microscopy.

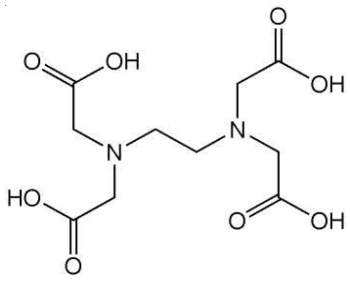

Fig. 1. Structure of EDTA

EXPERIMENTAL

Preparation of the specimens: Carbon steel specimens (0.026 % S, 0.06 % P, 0.4 % Mn and 0.1 % C and rest iron) of the dimensions 1 cm × 4 cm × 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: Carbon steel specimens in triplicate were immersed in 100 mL of the sea water containing various concentrations of the inhibitor in presence and absence of Zn^{2+} for 3 days. The corrosion product cleaned with Clark's solution[24]. The parameter of the sea water is given in Table-1.

TABLE-1
PHYSICO-CHEMICAL PARAMETERS OF SEA WATER

Parameters	Value
pH	7.66
Conductivity	44200 μ mhos/cm
Chloride	16050 ppm
Sulphate	2616 ppm
TDS	30940 ppm
Total hardness	2800 ppm
Calcium	120 ppm
Sodium	6300 ppm
Magnesium	600 ppm
Potassium	400 ppm

The weights of the specimens before and after immersion were determined using a balance, Shimadzu AY62 model. Then the inhibition efficiency (IE) was calculated using the eqn. 1.

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

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:

$$CR = \frac{87.6\ W}{DAT}\ mm/y$$

where, W = weight loss in mgs, D = 7.87 g/cm^3, A = surface are of the specimen (10 cm^2) and T = 72 h.

Potentiodynamic polarization study: Polarization study was carried out in electrochemical impedance analyzer model CHI 660 A using a three electrode cell assembly. The working electrode was used as a rectangular specimen of carbon 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 ba 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 Ef (s) was zero and quiet time (s) was 2.

Surface examination study: The carbon steel specimens were immersed in various test solutions for a period of one day. After one day the specimens were taken out and dried. The nature of the film formed on the surface of metal specimens was analyzed by surface analysis technique, FTIR spectra and SEM.

FTIR spectra: The carbon steel specimens immersed in various test solutions for one day were taken out and dried. The film formed on the metal surface was carefully removed and thoroughly mixed with KBr, so as to make it uniform throughout. The FTIR spectra were recorded in a Perkin-Elmer 1600 spectrophotometer.

Scanning electron microscopy: The carbon steel specimens immersed in various test solutions for 1 day were taken out, rinsed with double distilled water, dried and subjected to the surface examination. The surface morphology measurements of the carbon steel surface were carried out by scanning electron microscopy using HITACHI S-3000H SEM.

RESULTS AND DISCUSSION

Analysis of results of weight loss study: The calculated inhibition efficiencies (IE) and corrosion rates of EDTA in controlling corrosion of carbon steel immersed in sea water both in absence and presence of Zn^{2+} ion are given in Table-2. The calculated value indicates the ability of EDTA to be a good corrosion inhibitor. The inhibition efficiencies is found to be enhanced in the presence of Zn^{2+} ion. EDTA alone shows some inhibition efficiencies. But the combination of 250 ppm EDTA and 50 ppm Zn^{2+} shows 96 % inhibition efficiencies. This suggests a synergistic effect exists between EDTA and Zn^{2+} [25-29].

TABLE-2
INHIBITION EFFICIENCIES (IE %) OBTAINED FROM EDTA-Zn^{2+} SYSTEMS, WHEN CARBON STEEL IMMERSED IN SEA WATER.
[corrosion rate (mm/y) given in the parantheses]
Inhibitor system: EDTA + Zn^{2+} Immersion period: 3 days

EDTA ppm	Inhibition efficiency (IE %)					
	Zn^{2+} (ppm)					
	0		25		50	
0	-	(0.1124)	12	(0.0989)	17	(0.0933)
50	12	(0.0989)	26	(0.0831)	34	(0.0741)
100	20	(0.0899)	38	(0.0696)	50	(0.0562)
150	32	(0.0764)	52	(0.0539)	68	(0.0359)
200	40	(0.0674)	74	(0.0292)	85	(0.0168)
250	48	(0.0584)	82	(0.0202)	96	(0.0045)

Analysis of polarization curves: The potentiodynamic polarization curves of carbon steel immersed in sea water in absence and presence of inhibitors are shown in Fig 2. 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 (Table-3). When carbon steel is immersed in sea water the corrosion potential is -731 mV *vs*. saturated calomel electrode (SCE). The corrosion current is 380×10^{-6} A/cm^2. When EDTA (250 ppm) and Zn^{2+} (50 ppm) are added to the above system the corrosion potential is shifted to the cathodic side (from -731 mV to -779 mV). This suggests that the cathodic reaction is controlled predominantly. The increase in both anodic and

TABLE-3
CORROSION PARAMETERS OF CARBON STEEL IMMERSED IN SEA WATER IN THE ABSENCE AND PRESENCE OF INHIBITORS OBTAINED BY POLARIZATION METHOD

EDTA (ppm)	Zn^{2+} (ppm)	E_{corr} (mV *vs* SCE)	b_c (mV/decade)	b_a (mV/decade)	LPR (Ω cm^2)	I_{corr} (A/cm^2)
0	0	- 731	135.5	162.3	1.0756×10^4	380×10^{-6}
250	50	- 779	156.7	183.0	1.6086×10^4	290×10^{-6}

cathodic Tafel slopes indicates that the inhibitor functions as mixed inhibitor. More over in presence of the inhibitor system, the corrosion current decreases from 380×10^{-6} A/cm^2 to 290×10^{-6} A/cm^2 and LPR value increases from 1.0756×10^4 Ω cm^2 to 1.6086×10^4 Ω cm^2. These observations indicate the formation of protective film on the metal surface[30-33].

Analysis of FTIR spectra: The FTIR spectrum of pure EDTA is shown in Fig. 3(a). The C-N and C=O stretching frequency of carboxyl group appear 1201 cm^{-1} and 1629 cm^{-1} respectively. The FTIR spectrum of the film formed on metal surface after immersion in sea water consisting EDTA (250 ppm) and Zn^{2+} (50 ppm) is shown in Fig. 3(b). The C-N stretching frequency has shifted from 1201 to 1114 cm^{-1}. The C=O stretching frequency shifted from 1629 cm^{-1} to 1637 cm^{-1}. This indicates that EDTA has coordinated to the Fe^{2+} on the anodic sties of the metal surface. The peak at 1392 cm^{-1} is due to Zn -O stretching. The -OH stretching frequency appears at 3418 cm^{-1}. These observations indicate the presence of $Zn(OH)_2$ formed on the metal surface. Thus FTIR study leads to the conclusion that the protective film consists of Fe^{2+}-EDTA complex and $Zn(OH)_2$ [21,22,34-40].

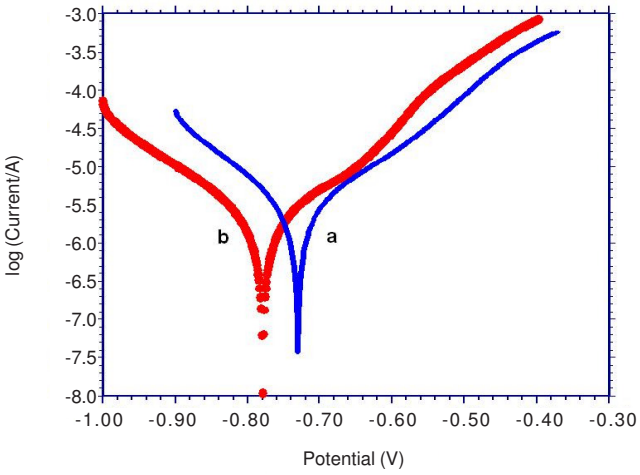

Fig. 2. Polarization curves of carbon steel immersed in various test solutions (a) Sea water (b) Sea water + EDTA (200 ppm) + Zn^{2+} (50 ppm)

Scanning electron microscopy: 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 micrographs (X 250, X 500) of polished carbon steel surface (control) in Fig. 4. (a, b) 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 250, X 500) of carbon steel specimen immersed in the sea water for one day in the absence and presence of inhibitor system are shown in Fig. 4. (c, d) and Fig. 4. b(e, f) respectively. The SEM micrographs of carbon steel surface immersed in sea water in Fig. 4. (c, d) shows the roughness of the metal surface, which indicates the corrosion of carbon steel in sea water. Fig. 4. (e, f) indicates that in the presence of 250 ppm EDTA and 50 ppm Zn^{2+} mixture in sea water, the surface coverage increases which in turn results in the formation of insoluble complex on the surface of the metal. In the presence of EDTA and Zn^{2+}, the surface is covered by a thin layer of inhibitors which effectively control the dissolution of carbon steel[41-44].

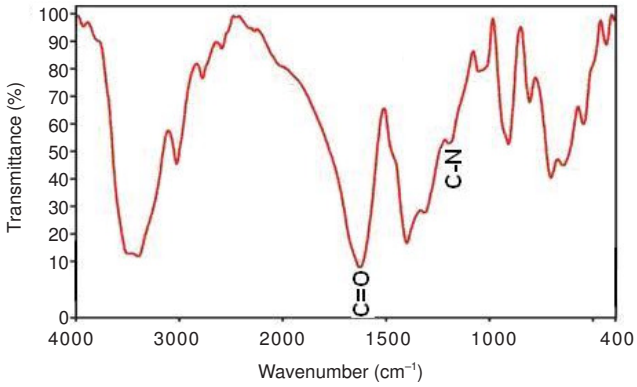

Fig. 3(a). FTIR Spectrum of pure EDTA

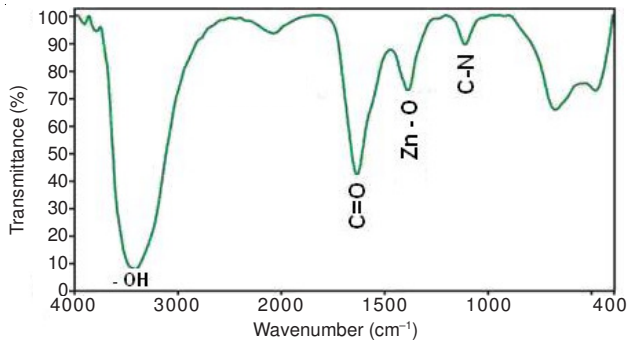

Fig. 3(b). FTIR Spectrum of the film formed on the metal surface

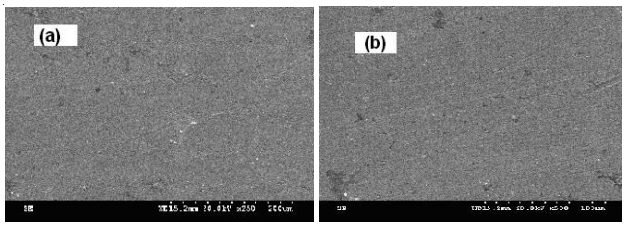

Fig. 4. SEM micrographs of polished carbon steel (control); (a) Carbon steel (control); Magnification-X 250; (b) Carbon steel (control); Magnification-X 500

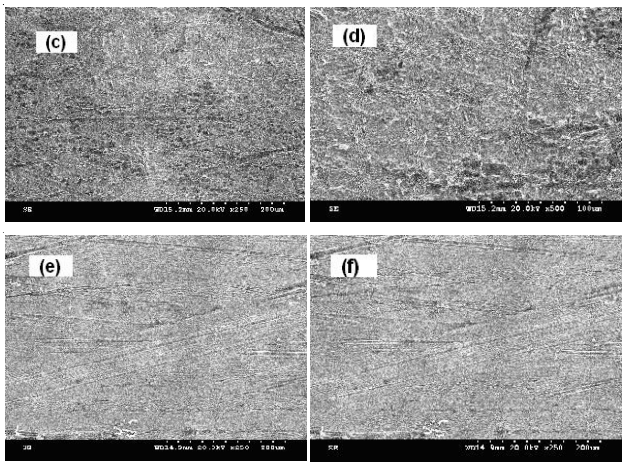

Fig. 4. SEM micrographs of carbon steel immersed in various test solutions; (c) Carbon steel immersed in sea water; Magnification-X 250; (d); Carbon steel immersed in sea water; Magnification-X 500; (e) Carbon steel immersed in sea water containing EDTA (250 ppm) + Zn^{2+} (50 ppm); Magnification-X 250; (f) Carbon steel immersed in sea water containing EDTA (200 ppm) + Zn^{2+} (50 ppm); Magnification-X 500

Mechanism of corrosion inhibition: With these discussions, a mechanism is proposed for the corrosion inhibition of carbon steel immersed in sea water by 250 ppm EDTA and 50 ppm Zn^{2+} system.

(1) When the formulation consisting of 250 ppm of EDTA and 50 ppm of Zn^{2+} in sea water there is a formation of EDTA - Zn^{2+} complex in solution.

(2) When carbon steel is immersed in this solution EDTA - Zn^{2+} complex diffuses from the bulk of the solution towards the metal surface.

(3) EDTA-Zn^{2+} complex is converted into EDTA-Fe^{2+} complex on the anodic sites of the metal surface with the release of Zn^{2+} ion.

$$Zn^{2+} - EDTA + Fe^{2+} \rightarrow Fe^{2+} - EDTA + Zn^{2+}$$

(4) The released Zn^{2+} combines with OH^- to form $Zn(OH)_2$ on the cathodic sites of the metal surface.

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

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

(6) In near neutral aqueous solution the anodic reaction is the formation of Fe^{2+}. This anodic reaction is controlled by the formation of EDTA-Fe^{2+} complex on the anodic site of the metal surface. The cathodic reaction is the generation of OH. It is controlled by formation of $Zn(OH)_2$ on the cathodic sites of the metal surface.

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

$$H_2O + ½\ O_2 + 2e^- \rightarrow 2\ OH^- \text{ (Cathodic reaction)}$$

$$Fe^{2+} + EDTA \rightarrow Fe^{2+} - EDTA \text{ complex}$$

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

(7) This accounts for the synergistic effect of EDTA-Zn^{2+} system.

Conclusion

The present study leads to the following conclusions:

(1) The inhibition efficiency of EDTA in controlling corrosion of carbon steel immersed in sea water in the absence and presence of Zn^{2+} has been evaluated by weight loss method.

(2) The formulation consisting of 250 ppm EDTA and 50 ppm Zn^{2+} has 96 % corrosion inhibition efficiency.

(3) Polarization study reveals that EDTA-Zn^{2+} system functions as mixed inhibitor.

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

(5) The SEM micrographs confirm the formation of protective layer on the metal surface.

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