ELECTROCHEMICAL AND SURFACE ANALYSIS STUDIES ON CORROSION INHIBITION OF CARBON STEEL

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The corrosion inhibition of inhibitor tris(hydroxymethyl)amino methane (THAM) and 1-hydroxyethylidenediphosphonic acid (HEDP) in combination with a bivalent cation like Zn^{2+} in controlling corrosion of carbon steel immersed in aqueous solution containing 60 ppm Cl⁻ was investigated using weight loss method and electrochemical impedance spectroscopy .The combined corrosion inhibition efficiency offered by 50 ppm of THAM, 250 ppm of HEDP, 50 ppm of Zn^{2+} has 86%. The synergistic effect of the inhibiting compound was calculated. The corrosion inhibition was observed due to the formation of more stable and compact protective film on the metal surface. Fluorescence spectral analysis was used in detecting the presence of iron-inhibitor complex and the coordination sites of the metal inhibitor with iron were determined by the FTIR spectra. The surface morphology of the protective film on the metal surface was characterized by using Scanning Electron Microscope (SEM)

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Introduction

Corrosion is the gradual destruction of material, usually metal, by chemical reaction with its environment. Phosphonates in combination with zinc ions have been in use as effective corrosion inhibitors for carbon steel in cooling water systems for the past three decades.[1-2] Several compounds such as nitrite, phosphate, [3-4] silicates, [5] sodium salicylate,[6] sodium cinnamate,[7] molybdate,[8-9] phosphonic acids,[10-12] polyacrylamide[13] and caffeine[14-15] have been used as corrosion inhibitors. Several phosphonic acids have been used as corrosion inhibitor along with metal cation such as Zn^{2+}.[16-18] Phosphonates are derivatives of phosphonic acids that contain direct phosphorous-to carbon bonds (P-C). The P-C bonds are more resistant to hydrolysis than the P-O-C bonds of organic phosphates. Phosphonic acids are used as scale inhibitors in. aqueous Systems.[19-20] Phosphonic acids are extensively used now-a-days due to their complex-forming abilities, high stability under harsh conditions and low toxicity. The inhibition efficiency of phosphonates depends on the number of phosphono groups in a molecule and also on different substituents.

Electrochemical techniques have been used in corrosion inhibition studies of mild steel by phosphonic acid. [21-22] The aim of the present study was to investigate synergistic corrosion inhibition for THAM-Zn^{2+} and HEDP combination to carbon steel immersed in aqueous solution containing 60ppm Cl⁻. The corrosion inhibition efficiency was evaluated using mass loss method and the AC impedance spectra. The protective film formed on the metal surface characterized with the help of surface analytical techniques such as Fluorescence Spectra, Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM).

Materials and Methods

Preparation of mild steel 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 trichloroethylene and used for mass loss and surface examination studies. The environment chosen is an aqueous solution containing 60 ppm Cl⁻.

Determination of corrosion rate

The weighed specimen, in triplicate were suspended by means of glass hooks in 100 ml beakers containing 100 ml of an aqueous solution containing 60 ppm Cl⁻ containing various concentration of the inhibitors in the presence and absence of Zn^{2+} for 3 days of immersion. After 3 days of immersion the specimens were taken out, washed in running water, dried and weighed. From the change in weights of the specimen corrosion rates (*CR*) were calculated using the following relationship.

$$CR = \frac{\Delta m}{S\,t} \qquad (1)$$

where

   Δm - loss in weight (mg)

   S - surface area of the specimen (dm²)

   t - period of immersion (days)

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

586

$$IE = 100\left(1 - \frac{W_2}{W_1}\right) \qquad (2)$$

where

    W_1 = corrosion rate in the absence of the inhibitor and

    W_2 = Corrosion rate in the presence of the inhibitor

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 electrode. A time interval of 5 to 10 minutes 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} value can be calculated using the following relationship.

$$C_{dl} = \frac{1}{2\pi R_t f_{max}} \qquad (3)$$

Surface characterization studies

The carbon steel specimens were immersed in blank, as well as inhibitor solutions, for a period of three days. After three days, the specimen were taken out and dried. The nature of the film formed on the surface of the metal specimens was analysed by various analysis techniques.

FT-IR spectra

The 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.

Surface analysis by fluorescence spectroscopy

Fluorescence spectra of solutions and also the films formed on the metal surface were recorded using Jasco-F-6300 spectra fluorometer.

SEM Analysis

SEM provides a pictorial representation in the surface to understand the nature of the surface film in the absence and presence of inhibitors and extent of corrosion of carbon steel. The SEM micrographs of the surface are examined.

Results and Discussion

The corrosion rates (*CR*) of carbon steel immersed in aqueous solution containing 60 ppm Cl$^-$ and also inhibition efficiencies (*IE*) in the absence and presence of inhibitor THAM and HEDP obtained by weight loss method are given in Table 2. It is observed from Table 1 that THAM shows some inhibition efficiency. 50 ppm of THAM has 52% inhibition efficiency and 50 ppm of Zn^{2+} has 24% *IE*. Their combination has 62% *IE*.

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. Immersion period = 3 days, pH=8.84

Cl$^-$, ppm	THAM,ppm	Zn^{2+},ppm	CR, mdd	IE, %
60	0	0	23	-
60	0	50	17.48	24
60	50	50	8.74	62
60	100	50	11.04	52
60	150	50	13.34	42
60	200	50	13.57	41
60	250	50	13.80	40

It is observed that when HEDP is added, the inhibition efficiency of THAM-Zn^{2+} system increases. The increase in IE is more pronounced at 250 ppm of HEDP. Synergistic effect exists between THAM-Zn^{2+} system and HEDP (250 ppm). For example 50ppm of Zn^{2+} and 50ppm THAM has 62% IE. Their combination [THAM (50 ppm) - Zn^{2+} (50 ppm)-HEDP (250 ppm)] has 86% *IE*.

Table 2. 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. Immersion period = 3days, pH = 8.84

Cl$^-$, ppm	THAM,ppm	Zn^{2+},ppm	CR,mdd	IE, %
60	0	0	23	-
60	0	50	17.48	24
60	50	50	8.74	62
60	100	50	11.04	52
60	150	50	13.34	42
60	200	50	13.57	41
60	250	50	13.80	40

Synergism considerations

According to studies by Gomma[23] the synergism parameter (S_I) can be calculated using the relationship given by Aramaki and Hackmann.[24]

$$S_I = \frac{1 - \theta_{1+2}}{1 - \theta'_{1+2}} \qquad (4)$$

where

    $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$

    θ_1 = surface coverage for substance (HEDP)

    θ_2 = surface coverage for substance (THAM-Zn^{2+})

    θ'_{1+2} = surface coverage for combined substance (THAM-Zn^{2+} - HEDP), when θ is the surface coverage, *θ=IE/100*.

The values of synergism parameters are given in Table 3. It is observed that the value of synergism parameter is greater than 1.This suggests that a synergistic effect exists between THAM and Zn^{2+} (50 ppm) system and HEDP (250 ppm) when the value of synergism parameter is less than one. It is an indication that the synergistic effect is not significant.

Table 3 Inhibition efficiencies and synergism parameters for THAM-Zn^{2+}- HEDP systems, when carbon steel immersed in an aqueous solution containing 60 ppm Cl⁻; Immersion period 3 days, pH = 8.84

Cl⁻, ppm	THAM, ppm	Zn^{2+}, ppm	CR, mdd	IE, %
60	0	0	23	-
60	0	50	17.48	24
60	50	50	8.74	62
60	100	50	11.04	52
60	150	50	13.34	42
60	200	50	13.57	41
60	250	50	13.80	40

A=HEDP System; B = Zn^{2+} + THAM System; C = THAM-Zn^{2+}-HEDP System

Analysis of AC impedance spectra

AC impedance spectra of carbon steel immersed in aqueous solution containing 60 ppm Cl⁻ in the absence and presence of inhibitors are shown in Fig. 1 (Nyquist plots) and Fig. 2, Fig. 3 (Bode plots). The corrosion parameters namely charge transfer resistance and double layer capacitance derived from Nyquist plots are given in Table 4. The impedance (log Z ohm⁻¹) values derived from Bode plots are also given in Table 4. It is observed that when carbon steel immersed in an aqueous solution containing 60 ppm Cl⁻, the R_t value is 428 ohm cm². The C_{dl} value is 1.19×10^{-8} F cm⁻².The impedance value [log$Z$ ohm⁻¹] is 2.683.

When inhibitors (50 ppm of THAM + 50 ppm of Zn^{2+} + 250 ppm HEDP) are added the R_t value increases from 428 to 1716 ohm cm². The C_{dl} value decreased from 1.19×10^{-8} to 0.297×10^{-8} F cm⁻². The shape of the plot suggests that it is a diffusion controlled process. The impedance value increases from 2.683 to 3.90. This observation suggests that a protective film is formed on the metal surface**.**

Table 4. Corrosion parameters of carbon steel immersed in an aqueous solution containing 60 ppm of Cl⁻ obtained from AC impedance spectra*.* Immersion period 3 days, pH = 8.84

Cl⁻, ppm	THAM, ppm	Zn^{2+},ppm	CR, mdd	IE, %
60	0	0	23	-
60	0	50	17.48	24
60	50	50	8.74	62
60	100	50	11.04	52
60	150	50	13.34	42
60	200	50	13.57	41
60	250	50	13.80	40

D = Aqueous solution containing 60 ppm Cl⁻; E = THAM (50 ppm); Zn^{2+} (50 ppm); HEDP (250 ppm)
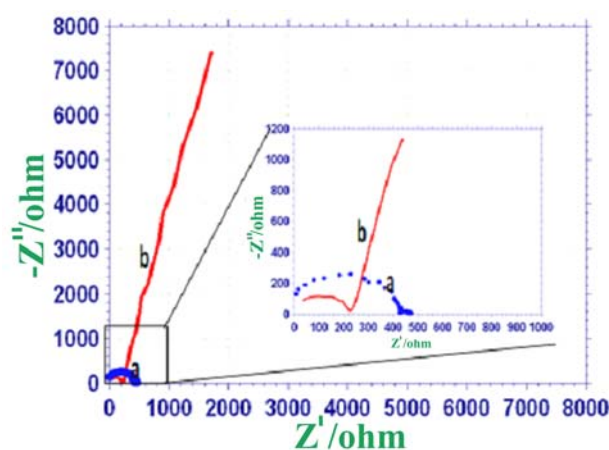

Figure 1. AC impedance spectra of carbon steel immersed in various test solutions (Nyquist Plot); a) 60 ppm Cl⁻ (blank); b) 60 ppm Cl⁻ + THAM (50 ppm) + Zn^{2+} (50 ppm) + HEDP (250 ppm)
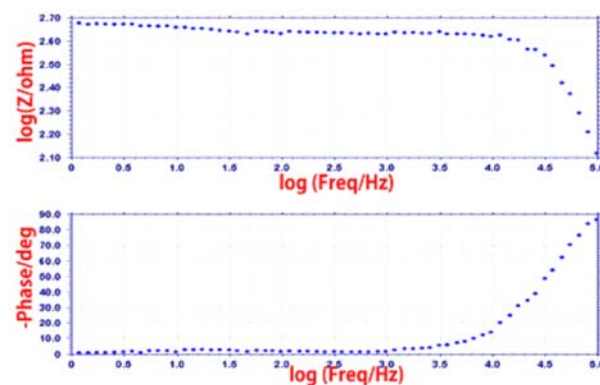

Figure 2. AC impedance spectra of carbon steel immersed in various test solutions (Bode Plot) a) 60 ppm Cl⁻ (Blank)
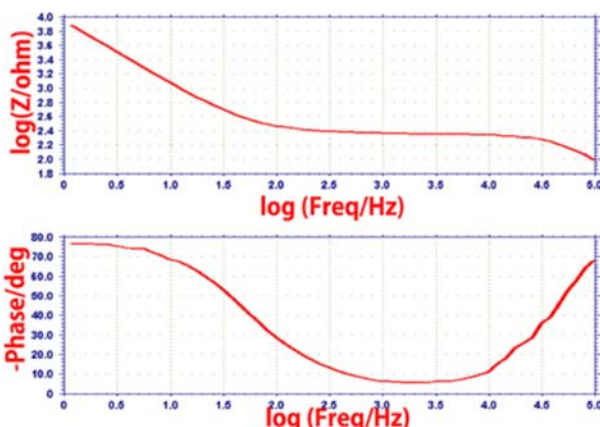

Figure 3. AC impedance spectra of carbon steel immersed in various test solutions (Bode Plot); a) 60 ppm Cl⁻ + THAM (50 ppm) + Zn^{2+} (50 ppm) + HEDP (250 ppm)

Analysis of the UV-Visible absorption spectra

The UV-Visible absorption a spectrum of an aqueous solution containing THAM and Fe^{2+} is shown in Figure 4. A peak appears at 305 nm. This is due to formation of THAM-Fe^{2+} complex in solution. When HEDP solution is added to the above solution, the intensity of the UV-Visible

588

absorption spectra slightly increases at 314 nm. This peak is due to formation of Fe^{2+}-HEDP complex and THAM-Fe^{2+} complex in solution. [25-26]
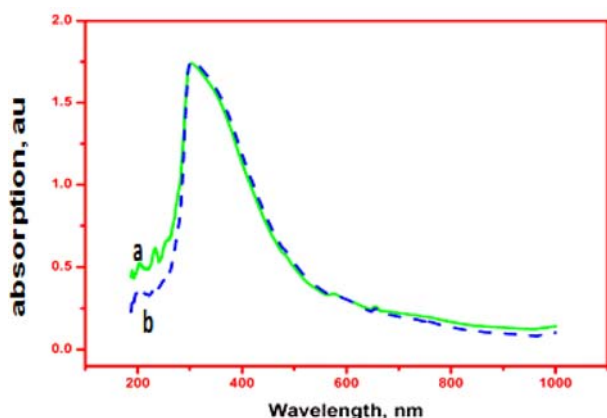

Figure 4. UV-absorption spectra solution containing a) THAM-Fe^{2+} system complex in solution; b) Fe^{2+}-THAM and Fe^{2+}-HEDP complex in solution (Fe^{2+}-THAM+HEDP solution)

Fluorescence spectra

The emission (λex 305nm) of solution containing THAM-Fe^{2+}-HEDP complex is shown in Figure 5. A peak appears at 314 nm. The emission spectrum of the film formed on the metal surface after immersion in solution containing 50 ppm of THAM, 50 ppm of Zn^{2+}, 250 ppm of HEDP is shown in Figure 5. A peak appears at 314 nm.

Hence, it is concluded that the protective film consists of Fe^{2+}-THAM complex and Fe^{2+}-HEDP complex, the number of peak obtained is only one. Hence it is informed that the complex of somewhat highly symmetric in solution. [27]
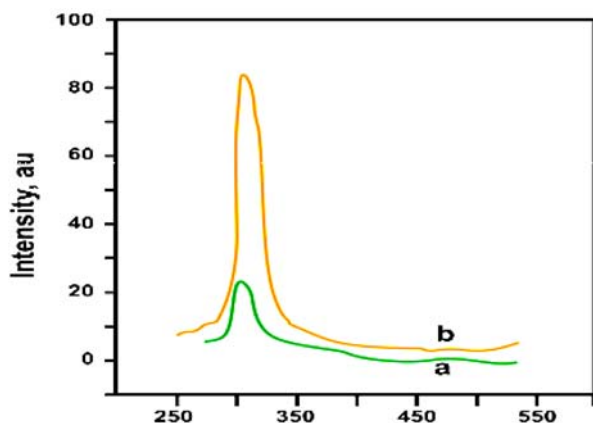

Figure 5. Fluorescence spectra, a) THAM-Fe^{2+}-HEDP complex in solution; b) Film formed on metal surface after immersion in solution containing 50 ppm of THAM and 50 ppm of Zn^{2+} and 250 ppm of HEDP

Analysis of FTIR spectrum

The FTIR spectra have been used to analyze the film formed on the metal surface. The FTIR spectrum of pure THAM is shown in Figure 6. The NH stretching frequency and –OH stretching frequency have overlapped and appears at 3350 cm^{-1}. The CN stretching frequency appears at 1042 cm^{-1}. FTIR spectrum of pure HEDP is shown in Figure 7.

The FTIR spectrum of the film formed on the metal surface after immersion in the solution containing 60 ppm Cl^-, 250 ppm HEDP 50 ppm THAM and 50 ppm of Zn^{2+} is shown in Figure 8. The P-O stretching frequency of HEDP has shifted from 1119 cm^{-1} to 1071cm^{-1}. [28-30] This indicates that the formation of Fe^{2+}-HEDP complex on the metal surface. The –OH stretching frequency has shifted from 3350 cm^{-1} to 3403 cm^{-1}. The C-N stretching frequency has shifted form 1042 cm^{-1} to 1021cm^{-1}. This suggests that HEDP and THAM have coordinated with Fe^{2+}, through their polar groups resulting in the formation of Fe^{2+}-HEDP complex and Fe^{2+}-THAM complex. The peak at 1384 cm^{-1} is due to Zn-O stretching. The –OH stretching frequency appears at 3350 cm^{-1}. There results suggest the formation of $Zn(OH)_2$ on metal surface. [31-35]
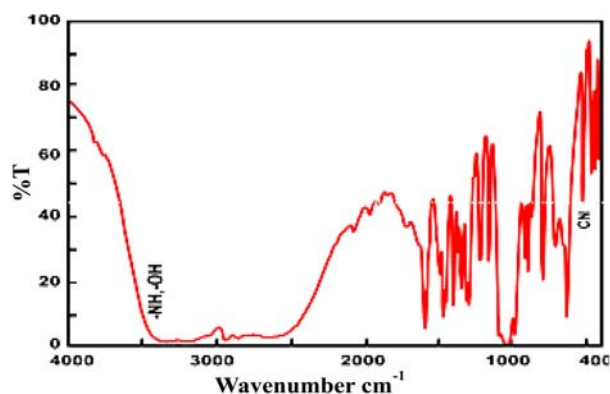

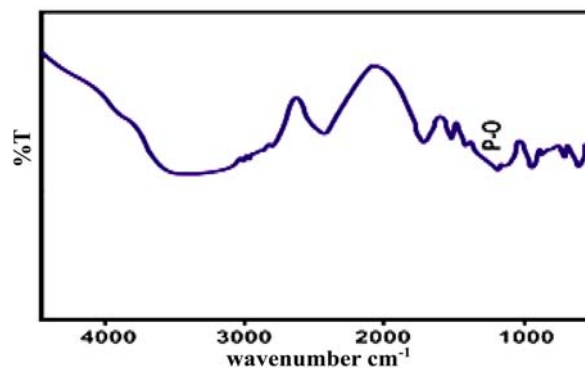**Figure 6.** IR spectrum of *p*ure THAM
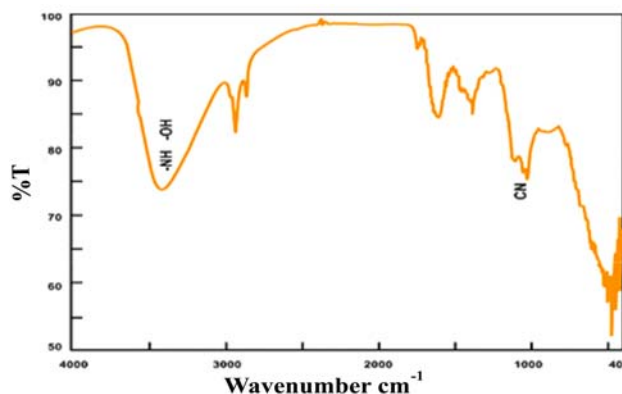

Figure 7. IR spectrum of pure HEDP

Figure 8. Film formed on carbon steel after immersion in aqueous solution containing Zn^{2+} + 250 ppm of HEDP

589

SEM analysis of metal surface

The SEM images of different magnification (X500,X1000) of carbon steel specimen immersed in aqueous solution contain 60 ppm of Cl^- for 3 days in the absence and presence are shown in Figure 9. This indicates that in the presence on 50 ppm THAM and 50 ppm Zn^{2+} and 250 ppm of HEDP, the surface coverage increases which in turn results in the formation of insoluble complex on the surface of the metal.[36] In the presence of THAM and Zn^{2+} and HEDP system the surface is covered by a thin layer of inhibitors which effectively control the dissolution of carbon steel Figure 10.
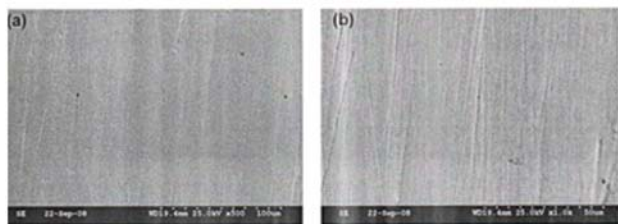

Figure 9. SEM micrographs of a) Carbon steel (control); Magnification-X 500; b) Carbon steel (control); Magnification-X 1000
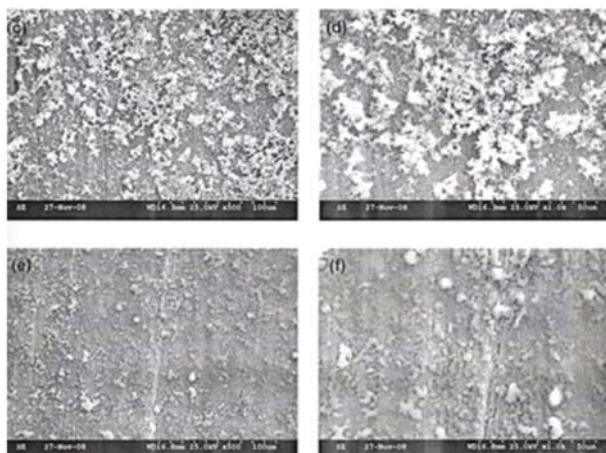

Figure 10. SEM micrographs of a) 60 ppm Cl^- Magnification-X 500; b) 60 ppm Cl^- Magnification-X 1000; c) THAM 50 ppm + Zn^{2+} 50 ppm + 60 ppm Cl^- + HEDP 250 ppm, Magnification – X500; d) THAM 50 ppm + Zn^{2+} 50 ppm + 60 ppm Cl^- + HEDP 250 ppm Magnification –X1000

Conclusion

The results of the weight loss study shows that the formulation consisting of 50 ppm THAM and 50 ppm of Zn^{2+} and 250 ppm HEDP has 86% of inhibition efficiency in controlling corrosion of carbon steel. AC impedance spectra reveal that the protective film formed on the metal surface. FTIR spectra reveal that the protective film consists of Fe^{2+}-THAM complex and Fe^{2+}- HEDP complex and $Zn(OH)_2$.

When carbon steel is immersed in solution containing 60 ppm of Cl^-, 50 ppm of THAM, 50 ppm of Zn^{2+} and 250 ppm of HEDP, the Zn^{2+}-THAM, Zn^{2+}-HEDP complex diffuses from the bulk of the solution towards metal surface.

On the metal surface Zn^{2+}-THAM-HEDP complex is converted in to Fe^{2+}-THAM, Fe^{2+}-HEDP complex on the anodic sites. Zn^{2+} is released.

$$Zn^{2+}\text{-}THAM, Zn^{2+}\text{-}HEDP + Fe^{2+} \rightarrow$$

$$Fe^{2+}\text{-}HEDP, Fe^{2+}\text{-}THAM + Zn^{2+}$$
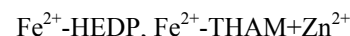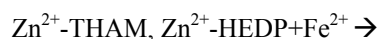
The released Zn^{2+} combines with OH^- to form $Zn(OH)_2$ on the cathodic sites .

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$$
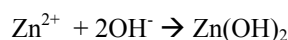
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591

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