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Eosin as Corrosion Inhibitor for Carbon Steel in Well Water

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Abstract: The inhibition efficiency of Eosin in controlling corrosion of carbon steel immersed in well water, has been evaluated by mass loss method both in absence and presence of zinc ion. A synergistic effect exists between Eosin (EN) and Zn^{2+}. The inhibition efficiency (IE) of the EN – Zn^{2+} system decreases with increase in immersion period. Addition of N-cetyl-N,N,N-trimethylammonium bromide (CTAB), sodium dodecyl sulphate (SDS), sodium sulphite (Na_2SO_3) does not change the excellent inhibition efficiency of the EN-Zn^{2+} system. Polarization study suggests that the EN-Zn^{2+} system functions as an anodic inhibitor system. AC impedance spectra reveal the presence of a protective film on the metal surface. FTIR spectra indicate that the protective film consists of Fe^{2+} - EN complex and $Zn(OH)_2$.

Keywords: Carbon steel, corrosion inhibition, eosin, dyes and synergistic effect.

INTRODUCTION

Several compounds such as molybdate [1, 2] phosphonic acids [3], poly acrylamide [4] and caffeine [5, 6] have been used as corrosion inhibitors. Corrosion inhibition of mild steel in acidic media by some organic dyes has been investigated [7]. Oguzie has studied the inhibition of corrosion of mild steel in hydrochloric acid solution by methylene blue dye [8]. Eriochrome Black–T serves as a good corrosion inhibitor for carbon steel in well water [9]. At pH 11 methyl orange along with Zn^{2+} functions as a good inhibitor in controlling corrosion of aluminium [10] Madkour, has studied the kinetics of substituted bis and monoazodyes as corrosion inhibitors for aluminium in hydrochloric acid and sodium hydroxide solutions [11]. Oguzie, has studied the inhibition of aluminium, corrosion in potassium hydroxide by "Congored" dye and synergistic action with halide ions" [12]. The inhibition effect of New, Fuchsin dye on the corrosion of mild steel in HCl has been studied using electrochemical noise measurements (ENM) and the electrochemical impedance spectroscopy (EIS) method [13]. Though several dyes have been used as corrosion inhibitors, the mechanistic aspects of corrosion inhibition have not been studied in detail. This prompted us to investigate (i) the inhibition efficiency of Eosin in controlling the corrosion of carbon steel immersed in well water in the absence and presence of zinc ion (ii) the influence of pH and immersion period (iii) to analyze the protective film formed on the metal surface by FTIR spectroscopy (iv) to propose a suitable mechanism of corrosion inhibition based on the results of electrochemical studies such as polarization and AC impedance and FTIR spectra.

EXPERIMENTAL METHODS

Preparation of the Specimens

Carbon steel specimens (0.026% S, 0.06% P, 0.4% Mn, 0.1% C and the rest iron) of the dimensions 10 cm x 4.0 cm x 0.2 cm were polished to mirror finish and degreased with trichloroethylene and used for mass loss method and surface examination studies.

Mass Loss Method

Relevant data of the well water used in this study are given in Table **1**.

Table 1. Parameters of Well Water

Parameter	Value
pH	8.38
Conductivity	3110µ mhos / cm
TDS	2013 ppm
Chloride	665 ppm
Sulphate	14 ppm
Total hardness	1100 ppm

Carbon steel specimens, in triplicate were immersed in 100 ml of well water and various concentrations of Eosin in the presence and absence of Zn^{2+} (as $ZnSO_4.7H_2O$) for a period of one day. The corrosion products were cleaned with Clarke's solution [14]. The weight of the specimens before and after immersion was determined using Shimadzu balance AY62. The corrosion inhibition efficiency was calculated with equation (1).

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

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.

Surface Examination Study

FTIR Spectra

The structure of Eosin is shown in Scheme **1**. The carbon steel specimens were immersed in various test solutions for one day. The specimens were taken from the test solutions and dried. The film formed on the metal surface was carefully removed and thoroughly mixed with KBr so as to make

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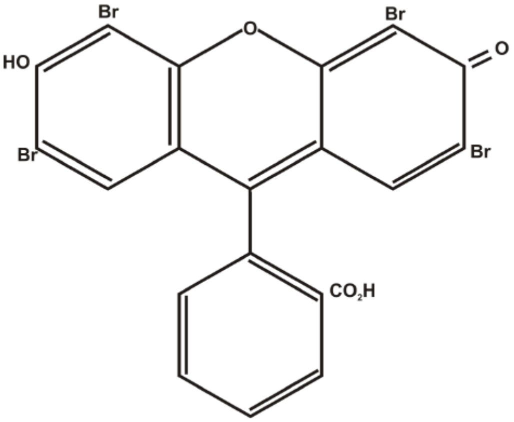
it uniform through out. The FTIR spectra were recorded in a Perkin – Elmer – 1600 spectrophotometer.



Scheme 1.

Potentio Dynamic Polarization Study

Polarization study was carried out in H and CH Electrochemical Impedance Analyzer model CHI660A using a three electrode cell assembly. Carbon steel was used as working electrode with platinum as counter electrode and saturated calomel electrode (SCE) as reference electrode. The corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) and Tafel slopes (anodic slope b_a and cathodic slope b_c) were calculated.

A.C. Impedance Spectra

A.C. impedance spectra were recorded in the same instrument used for polarization study using the same type of three electrode cell assembly. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms for various frequencies. The charge transfer resistance (R_t) and double layer capacitance (C_{dl}) values were calculated.

RESULTS AND DISCUSSION

Analysis of Results of Mass Loss Study

The calculated inhibition efficiencies (IE) of eosin in controlling the corrosion of carbon steel immersed in well water both in the absence and presence of zinc ion have been tabulated in Tables **2-5**. The calculated values indicate the ability of eosin to be a good corrosion inhibitor. The inhibition efficiency is found to be enhanced in the presence of zinc ion. Eosin alone shows some IE. But the combination of 60 ppm EN and 50 ppm of Zn^{2+} shows excellent IE. This shows that synergistic effect exists between EN of Zn^{2+}.

Table 2. Corrosion Rates (CR) of Carbon Steel in Well Water in the Absence and Presence of Inhibitors and the Inhibition Efficiencies Obtained by Mass Loss Method

EN ppm	Zn^{2+} ppm	CR mdd	IE %
0	0	59.09	--
20	0	53.18	10
60	0	50.23	15
100	0	49.04	17
140	0	48.45	18
180	0	47.27	20

Inhibitor system: Eosin + Zn^{2+}.
Immersion period: One day.

Table 3. Corrosion Rates (CR) of Carbon Steel in Well Water in the Absence and Presence of Inhibitors and the Inhibition Efficiencies Obtained by Mass Loss Method

EN ppm	Zn^{2+} ppm	CR mdd	IE %
0	0	59.09	--
20	10	10.05	83
60	10	8.86	85
100	10	3.55	94
140	10	2.95	95
180	10	2.36	96

Inhibitor System: Eosin + Zn^{2+}.
Immersion Period: One day.

Table 4. Corrosion Rates (CR) of Carbon Steel in Well Water in the Absence and Presence of Inhibitors and the Inhibition Efficiencies Obtained by Mass Loss Method

EN ppm	Zn^{2+} ppm	CR mdd	IE %
0	0	59.09	--
20	25	7.68	87
60	25	5.91	90
100	25	4.73	92
140	25	3.55	94
180	25	2.36	96

Inhibitor system: Eosin + Zn^{2+}.
Immersion period: One day.

Table 5. Corrosion Rates (CR) of Carbon Steel in Well Water in the Absence and Presence of Inhibitors and the Inhibition Efficiencies Obtained by Mass Loss Method

EN ppm	Zn^{2+} ppm	CR mdd	IE %
0	0	59.09	--
20	50	4.73	92
60	50	1.18	98
100	50	1.179	98
140	50	1.178	98
180	50	1.177	98

Inhibitor system: Eosin + Zn^{2+}.
Immersion period: One day.

Influence of Immersion Period on Inhibition Efficiency

The IE of EN (60 ppm) – Zn^{2+} (50 ppm) (Table **6**) system is found to decrease as the immersion period increases. This indicates that the protective film formed on the metal surface is unable to withstand the continuous attack of corrosive ions such as Cl^- ion (665 ppm) present in well water. There is a competition between the formations of $FeCl_2$ (and also $FeCl_3$) and Fe^{2+} -EN complex on the anodic sites of the metal surface. Perusal of the results suggests that the formation of $FeCl_2$ is favoured when compared with the formation of Fe^{2+}-EN complex [15, 16].

Table 6. Influence of Immersion Period on the Inhibition Efficiency of Eosin (60 ppm) + Zn^{2+} (50 ppm) System

Immersion Period (Day)	1	3	5	7
System: well water CR (mdd)	59.09	21.52	14.9	17
System: well water + EN (60 ppm) + Zn^{2+} (50 ppm) CR (mdd)	1.18	2.15	2.09	4.08
IE%	98	90	86	76

Inhibitor system: Eosin 60 ppm + Zn^{2+} (50 ppm) system.

Influence of N-Cetyl N,N,N-trimethyl Ammonium Bromide (CTAB) on the Inhibition Efficiency of En(60 ppm) – Zn^{2+} (60 ppm) System

The influence of CTAB on the inhibition efficiency of EN (60 ppm) – Zn^{2+} (50 ppm) system is given in Table **7**. It is interesting to find that the IE of the EN-Zn^{2+} system is not changed by the addition of CTAB. CTAB is a biocide. It can control the corrosion caused by bacteria. The present study reveals that the formulation consisting of EN, Zn^{2+} and CTAB has excellent corrosion inhibition efficiency. It is expected that this formulation will have excellent biocidal efficiency also. Hence this formulation may be used in cooling water system.

Table 7. Influence of N-Cetyl-N,N,N-Trimethyl Ammonium Bromide (CTAB) on the Inhibition Efficiency of EN + Zn^{2+} System

EN ppm	Zn^{2+} ppm	CTAB ppm	CR mdd	IE %
0	0	0	59.09	--
60	50	50	1.18	98
60	50	100	1.179	98
60	50	150	1.178	98
60	50	200	1.177	98
60	50	250	1.175	98

Inhibitor system: EN(60 ppm) + Zn^{2+} (50 ppm) + CTAB.
Immersion period: One day.

Influence of Sodium Dodecyl Sulphate (SDS) on the Inhibition Efficiency of EN(60 ppm) – Zn^{2+} (50 ppm) System

The influence of SDS on the inhibition efficiency of EN(60 ppm) – Zn^{2+} (50 ppm) system is given in Table **8**. The IE of EN-Zn^{2+} system is not changed by the addition of SDS. It can control the corrosion caused by bacteria. The present study reveals that the formulation consisting of EN, Zn^{2+} and SDS has excellent corrosion inhibition efficiency. It is expected that this formulation will have excellent biocidal efficiency also.

Table 8. Influence of Sodium Dodecyl Sulphate (SDS) on the Inhibition Efficiency of EN + Zn^{2+} System

EN ppm	Zn^{2+} ppm	SDS ppm	CR mdd	IE %
0	0	0	59.09	--
60	50	50	1.18	98
60	50	100	1.179	98
60	50	150	1.178	98
60	50	200	1.177	98
60	50	250	1.175	98

Inhibitor System: EN (60 ppm) + Zn^{2+} (50 ppm) + SDS.
Immersion Period: One day.

Influence of Sodium Sulphite (Na_2SO_3) on the Inhibition Efficiency of EN (60 ppm) – Zn^{2+} (50 ppm) System

The influence of Na_2SO_3 on the inhibition efficiency of EN-Zn^{2+} system is given in Table **9**. Addition of Na_2SO_3 has no influence on the inhibition efficiency of EN(60 ppm) + Zn^{2+} (50 ppm) system.

Table 9. Influence of Na_2SO_3 on the Inhibition Efficiency of EN + Zn^{2+} System

EN ppm	Zn^{2+} ppm	Na_2SO_3 ppm	CR mdd	IE %
0	0	0	59.09	--
60	50	50	1.18	98
60	50	100	1.179	98
60	50	150	1.178	98
60	50	200	1.177	98
60	50	250	1.175	98

Inhibitor system: EN (60 ppm) + Zn^{2+} (50 ppm) + Na_2SO_3.

Influence of pH on Inhibition Efficiency

The IE of the EN-Zn^{2+} system has been studied at different pH of the solutions and it is calculated. IE values have been tabulated in Table **10**. At pH6 the IE is found to be 85%. This decrease in IE is due to the fact that the protective film formed on the metal surface is broken by the attack of H^+ ions. At pH8 the IE is 98%. Further increase in pH of the solution lowers IE substantially. Experimental results suggest that the amount of Zn^{2+} available to transport EN towards the metal surface decreases at high pH. This may be due to the fact that zinc ions in the bulk of the solution might have precipitated as zinc hydroxide.

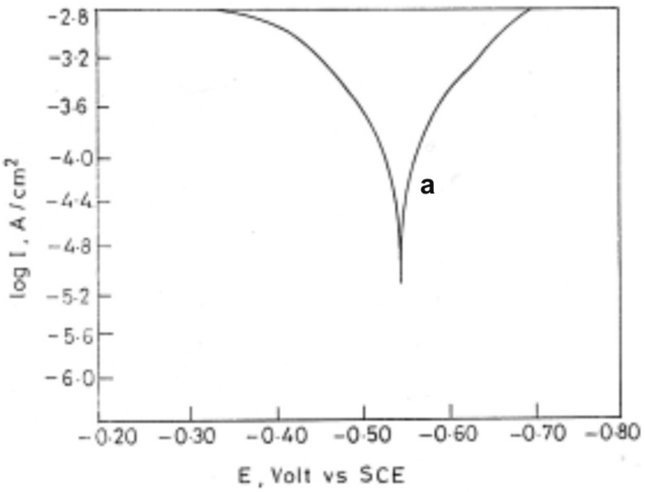
Analysis of Polarization Curves

The potentiodynamic polarization curves of carbon steel immersed in well water in the absence and presence of inhibitors are shown in Fig. (**1a-c**). The corrosion parameters are given in Table **11**. When carbon steel is immersed in well water the corrosion potential is -550 mV *vs* SCE (saturated Calomel Electrode). The corrosion current is 5.2480 x 10^{-4} A/cm^2. When EN(60 ppm) and Zn^{2+} (50 ppm) are added to the above system the corrosion potential shifts to the anodic side (-546 mV *vs* SCE). This suggests that this formulation controls the anodic reaction predominantly. In the presence of this inhibitor system, the corrosion current decreases from 5.2480 x 10^{-4} A/cm^2 to 4.9442 x 10^{-5} A/cm^2. This suggests the inhibitive nature of this inhibitor system.

Table 10. Influence of Various pH on the Inhibition Efficiency of EN + Zn^{2+} System

pH	6	8	11
System: Well Water CR (mdd)	17.27	59.09	3.64
System: Well water + EN (60 ppm) + Zn^{2+} (50 ppm)			
CR (mdd)	2.59	1.18	0.36
IE%	85	98	90

Inhibitor system: EN (60 ppm) + Zn^{2+} (50 ppm).
Immersion period: One day.



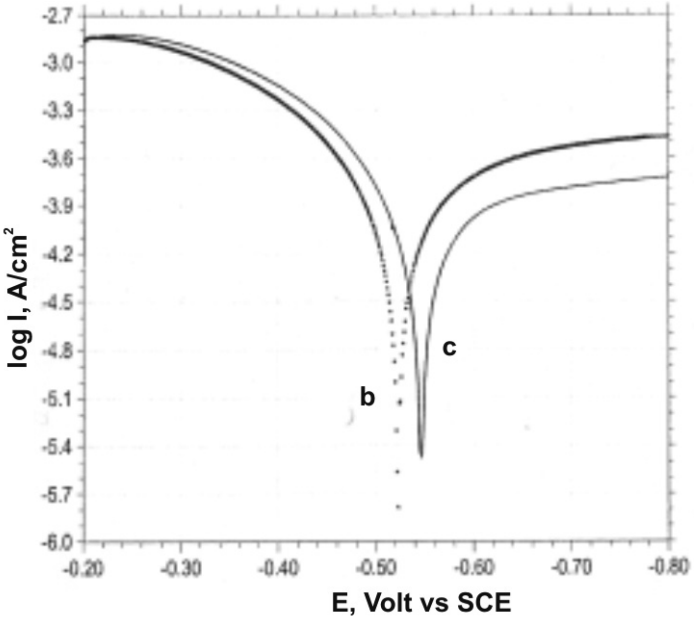


Fig. (1). Polarisation curves of carbon steel immersed in test solution. (**a**) Well water, (**b**) Well water + EN (60 ppm), (**c**) Well water + EN (60 ppm) + Zn^{2+} (50 ppm).

Table 11. Corrosion Parameters of Carbon Steel Immersed in Well Water in the Absence and Presence of Inhibitors

EN ppm	Zn^{2+} ppm	E_{corr} mV *vs* SCE	b_a mV	b_c mV	I_{corr} A/cm^2
0	0	-550	115	125	5.2480 x 10^{-4}
60	0	-521	157	314	5.1405 x 10^{-4}
60	50	-546	86	175	4.9442 x 10^{-5}

Inhibitor: EN (60 ppm) + Zn^{2+} (50 ppm).

Analysis of AC Impedance Spectra

The AC impedance spectra of carbon steel under our study are shown in Fig. (**2a-c**). The impedance parameters have been tabulated in Table **12**. When carbon steel is immersed in well water the charge transfer resistance R_t is 59.6 ohm cm^2. The double layer capacitance C_{dl} is 4.8854 x 10^{-8} µF/cm^2. When the formulation consisting of EN and Zn^{2+} is added the R_t value increases to 70.64 and C_{dl} value decreases to 4.127 x 10^{-8} µF/cm^2. This increase in charge transfer resistance value (R_t) and the decrease in the double layer capacitance value (C_{dl}) confirms the formation of a protective film on the surface of the metal. This accounts for the better inhibition efficiency of the EN-Zn^{2+} system.

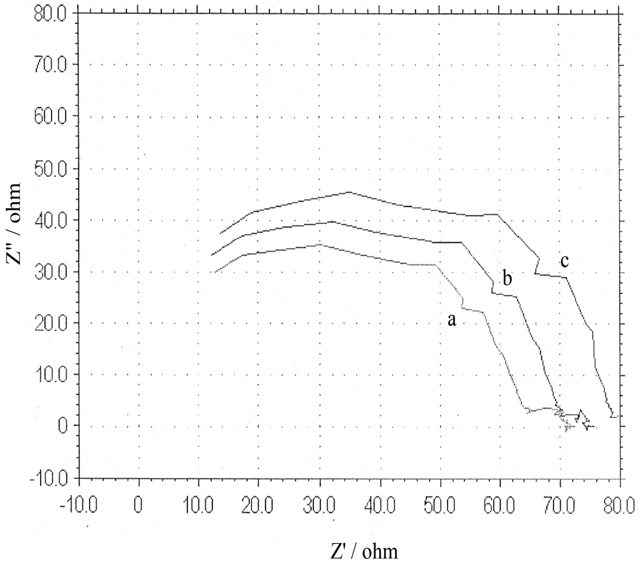


Fig. (2). AC impedance spectra of carbon steel immersed in test solution. (**a**) Well water, (**b**) Well water + EN (60 ppm), (**c**) Well water + EN (60 ppm) + Zn^{2+} (50 ppm).

Table 12. AC Impedance Parameters of Carbon Steel Immersed in Well Water in the Absence and Presence of Inhibitors

EN ppm	Zn^{2+} ppm	R_t ohm cm^2	C_{dl} µF / cm^2
0	0	59.6	4.8854 x 10^{-8}
60	0	62.39	4.6668 x 10^{-8}
60	50	70.64	4.127 x 10^{-8}

Inhibitors: EN (60 ppm) + Zn^{2+} (50 ppm).

Analysis of FTIR Spectra

The FTIR spectra (KBr) of pure Eosin is shown in Fig. (**3a**). The FTIR spectrum (KBr) of the film formed on the surface of the carbon steel after immersion in solution containing 60 ppm of EN and 50 ppm of Zn^{2+} is shown in Fig. (**3b**). The C-Br stretching frequency shifts from 561 cm^{-1} to 494 cm^{-1}. The C=O stretching frequency shifts from 1645 cm^{-1} to 1629 cm^{-1}. In 3a the COOH stretching frequency occurs at 2343 cm^{-1}. In 3b the COOH stretching frequency is merged. The C-O-C stretching frequency shifts from 1080 cm^{-1} to 1022 cm^{-1}. It was inferred that Eosin has coordinated with Fe^{2+} through oxygen atom of carboxyl oxygen, COOH group and C-SO-C group resulting in the formation of Fe^{2+}-EN complex on the anodic sites of the metal surface. The band at 1392 cm^{-1} is due to $Zn(OH)_2$ formed on the cathodic sites of the metal surface [17,18]. Thus FTIR spectral study leads to the conclusion that the protective film consists of Fe^{2+} - EN complex and $Zn(OH)_2$.

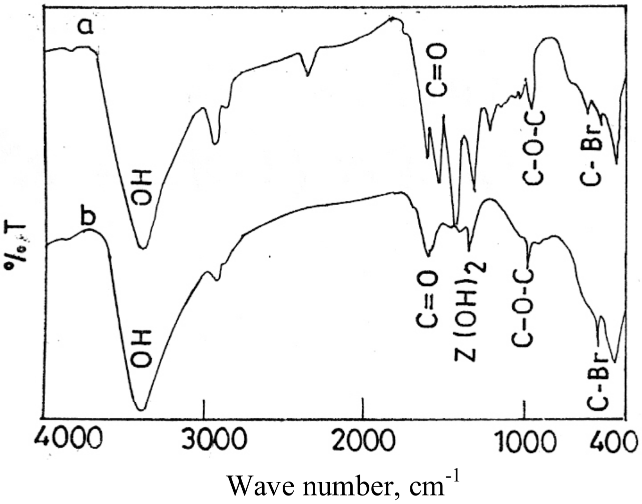


Fig. (3). FTIR spectra (KBr) of pure EN (**a**) and of film formed on the surface of film formed on the surface of the metal immersed in test solution (**b**). (**a**) Pure EN, (**b**) EN (60 ppm) + Zn^{2+} (50 ppm).

Mechanism of Corrosion Inhibition

With these discussions, a mechanism may be proposed for the corrosion inhibition of carbon steel immersed in well water by EN (60 ppm) – Zn^{2+} (50 ppm) system.

1. When the formulation consisting of 60 ppm of EN and 50 ppm of Zn^{2+} in well water there is formation of EN-Zn^{2+} complex in solution.
2. When carbon steel is immersed in this solution EN-Zn^{2+} complex diffuses from the bulk of the solution towards the metal surface.
3. EN-Zn^{2+} complex is converted into EN-Fe^{2+} complex on the anodic sites of the metal surface with the release of zinc ion.

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

   $Zn^{2+} + 2OH^-$ ------------> $Zn(OH)_2 \downarrow$
5. Thus the protective film consists of EN-Fe^{2+} 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 EN-Fe^{2+} complex on the anodic site of the metal surface. The cathodic reaction is the generation of OH^- which is controlled by the formation of $Zn(OH)_2$ on the cathodic sites of the metal surface.

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

   $2H_2O + O_2 + 4e^-$ ------------> $4OH^-$ (Cathodic reaction)
7. This accounts for the synergistic effect of EN-Zn^{2+} system.

CONCLUSIONS

To summarize, Eosin acts as a corrosion inhibitor system for carbon steel in well water. Its efficiency increased due to the transport ability of zinc ion through the formation of the EN-Zn^{2+} complex. A suitable mechanism has been proposed for the corrosion inhibition based on the results of electrochemical studies such as polarization and AC impedance and FTIR spectra. Perusal of the spectral analysis suggests that the protective film consists of Fe^{2+}-EN complex at the anodic sites and $Zn(OH)_2$ at the cathodic sites on the metal surface, which confirms that EN-Zn^{2+} system functions as an anodic inhibitor system.

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