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Research Article

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Sodium nitrite as corrosion inhibitor for mild steel in simulated concrete pore solution

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ABSTRACT

The corrosion inhibition effect of mild steel in simulated concrete pore solution (SCPS) by Sodium Nitrite and Zn^{2+} *has been investigated using weight loss method and cyclic voltammetry. The results show that 93% of inhibition efficiency is achieved with binary system consisting of 100 ppm of sodium nitrite – 50 ppm of* Zn^{2+} *. Surface evaluation technique like FTIR is used to determine the nature of the protective film formed on the metal surface. The protective film consists of* Fe^{2+} *- SN complex,* Zn^{2+}*- SN complex and* $Zn(OH)_2$*. Cyclic voltammetry study reveals that the protective film is more compact and stable even in 3.5% NaCl environment.*

Key words: *Concrete Corrosion, Simulated Concrete Pore Solution, Mild Steel, Sodium nitrite, Well water.*

INTRODUCTION

Effect of organic inhibitors on chloride corrosion of steel rebars in alkaline pore solution has been investigated by Marina Cabrini et al., The inhibition properties of aspartic and lactic acid salts are compared with nitrite ions with regard to their effect on critical chloride concentration. The tests were carried out on carbon steel specimens in simulated pore solutions with initial pH in the range of 12.6 to 13.8. The results confirm that 0.1 M aspartate exhibits an inhibiting effect comparable with nitrite ions of the same concentration[1].The inhibition of corrosion of reinforcing steel in simulated concrete pore solution (SCPS) has been studied using mass loss, gasometric measurements, potentiodynamic polarization and impedance studies using Mezlocillin (MZN) as a green inhibitor. The studies clearly revealed that MZN acted as cathodic inhibitor. Diffused reflectance spectra confirmed the formation of adsorbed film of inhibitor on reinforcing steel in SCPS[2].The corrosion inhibition effect and mechanism of D-sodium gluconate for reinforcing steel in the simulated concrete pore solution containing Cl^- were studied by electrochemical techniques, including corrosion potential, potentiodynamic polarization, and electrochemical impedance spectroscopy measurements. The results indicate that 0.01 M D-sodium gluconate showed a good corrosion inhibition effect on reinforcing steel in the simulated concrete pore solution containing 0.1 M NaCl because it strongly hindered the anodic reactions, by forming a compact adsorptive film by strong chelation and effectively inhibit the initiation of reinforcing steel corrosion[3].The Effect of NO_2^- on the early stages of pitting corrosion of Q235 carbon steel in a simulated concretepore solution (pH=11) was studied by means of polarization curves, Mott-Schottky curves and XPS methods. It was found that, NO_2^-inhibits both the stable pitting corrosion and the meta stable pitting corrosion [4]. The newly synthesized polymer, azo methine-based polyester, has been employed as inhibitor against the corrosion of rebar in artificially simulated concrete pore solution with chloride contamination (blank) by means of Tafel polarization and electrochemical impedance measurements. Polarization studies exhibited the maximum inhibition efficiency of 98% at 1000 ppm concentration. Electrochemical studies revealed the mixed-type nature of the inhibitors [5].

EXPERIMENTAL SECTION

2.1.Preparation of the specimens: Mild steel specimen was used in the present study. (Composition (wt %): 0.026 S, 0.06 P, 0.4Mn, 0.1C and balance iron. The dimension of the specimen was 1 x 4 x 0.2cm were polished to a mirror finish and degreased with trichloroethylene and used for the weight-loss method and surface examination studies. The environment chosen is well water and the physic-chemical parameter of well water is given in table 1.

2.2.Preparation of Simulated Concrete pore solution (SCPS): Simulated concrete pore solution is mainly consisted of saturated calcium hydroxide $Ca(OH)_2$, sodium hydroxide(NaOH) and potassium hydroxide (KOH) with the pH ~ 13.5. However in numerous studies of rebar corrosion, saturated $Ca(OH)_2$ has been used as a substitute for pore solution. A saturated calcium hydroxide solution is used in present study, as SCP solution with the pH ~ 12.5.

Table – 1 Physico- chemical parameters of well water

Parameters	value
pH	8.38
Conductivity	$1770 \mu\Omega^{-1}cm^{-1}$
Chloride	665 ppm
Sulphate	214 ppm
TDS	1100 ppm
Total hardness	402 ppm
Total Alkalinity	390 ppm
Magnesium	83 ppm
Potassium	55 ppm
Sodium	172 ppm
Calcium	88 ppm

2.3.weight loss method

Weighing the specimens before and after Corrosion: All the weighing of the mild steel specimens before and after corrosion was carried out using Shimadzu balance, model AY62.

Determination of Corrosion Rate: The weighed specimens in triplicate were suspended by means of glass hooks in 100 ml SCPS prepared in well water containing various concentration of potassium chromate in the presence and absence of Zn^{2+} for one day, the specimen were taken out, washed in running water, dried, and weighed. From the change in weights of the specimens, corrosion rates were calculated using the following relationship:

$$CR = [(\text{Weight loss in mg}) / (\text{Area of the specimens in dm}^2 \times \text{Immersion periods in days})]\ \text{mdd} \quad (1)$$

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

$$I.E = 100[1-(W_2/W_1)]\ \% \quad (2)$$

Where, W1= corrosion rate in the absence of the inhibitor, and W_2 = corrosion rate in the presence of the inhibitor,

RESULTS AND DISCUSSION

Analysis of results of the weight loss method

The calculated inhibition efficiencies(IE) and corrosion rates(CR) of sodium nitrite in controlling corrosion of mild steel immersed in simulated concrete pore solution(SCPS) for a period of one day in the absence of and presence of Zn^{2+} ion are given in Table 2. The inhibition efficiency is also given in this Table 2. The corrosion rates of the potassium chromate systems at various concentrations are shown in Fig 1.

It is observed from Table 2 that sodium nitrite (SN) shows some inhibition efficiency. 50 ppm of SN has 85% IE. As the concentration of SN increases, the IE increases, and corrosion rate decreases. 50 ppm of SN has 85% IE.100 ppm of SN has 93% IE. When 50 ppm of Zn^{2+} is added, the IE shifting increases in each case. That is addition of SN and Zn^{2+} increases the corrosion protection of mild steel immersed in SCPS prepared in well water.

Table 2: Inhibition efficiencies (IE%) and corrosion rates (CR) obtained from SN-Zn^{2+} system in controlling corrosion of mild steel immersed in SCPS prepared in well water

Inhibitor system: SN -Zn^{2+} Immersion period: 1 day

SN ppm	Zn^{2+} ppm	IE %	CR mdd
0	0	0	25
0	50	20	20
50	0	85	3.7
100	0	87	3.2
50	50	90	2.5
100	50	93	1.7

Influence of Zn^{2+} on the corrosion inhibition efficiency:

It is observed that when 50 ppm Zn^{2+} is added, the inhibition efficiency increases in the both the cases. The formulation consisting of SCPS + 100 ppm of sodium Nitrite and 50 ppm of Zn^{2+} has 90% corrosion inhibition efficiency. In presence of Zn^{2+} more amount sodium Nitrite is transported towards mild steel surface. On the mild steel Fe^{2+}- Nitrite complex is formed on the anodic sites of the mild steel surface. Thus the anodic reaction is controlled. The cathodic reaction, the generation of OH^- is controlled by the formation of $Zn(OH)_2$ on the cathodic sites of the mild steel surface. Thus, the anodic reaction and cathodic reaction are controlled effectively.

$Fe \rightarrow Fe^{2+} + 2e^-$ (anodic reaction),

$Fe^{2+} + Zn^{2+}$ – Nitrite $\rightarrow Fe^{2+}$ – Nitrite + Zn^{2+}

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (cathodic reaction),

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

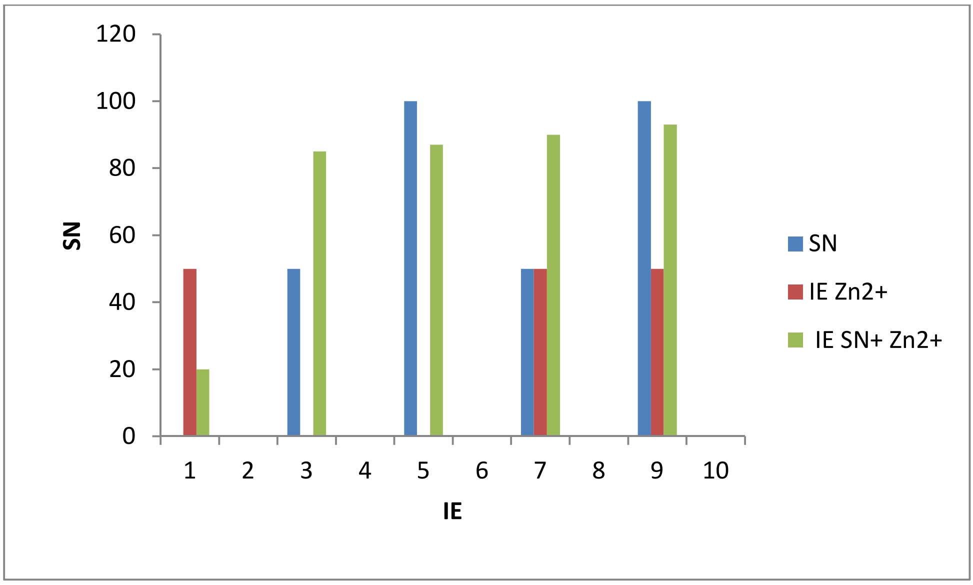

Fig.: Graph inhibition efficiency (IE) of SN – Zn^{2+} system in the corrosion of mild steel immersed in SCPS prepared in well water

Analysis of FTIR spectra

FTIR offers quantitative and qualitative analysis for organic and inorganic samples. Fourier Transform Infrared spectroscopy (FTIR) identifies chemical bonds in a molecule by producing on infrared absorption spectrum. The spectra produce a profile of the sample, a distinctive molecular fingerprint that can be used to screen and scan samples for many different components. FTIR is an effective analytical instrument for detecting functional groups and characterizing covalent bonding information.

FTIR spectra were used to analyze the protective film formed on metal surface [6]. The FTIR (KBr) spectrum of pure sodium nitrite is given in figure 2a. The NO_2^- stretching frequency appears at 1268 cm^{-1}. The FTIR spectrum of the film formed on the metal surface after immersion in SCPS prepared in well water containing 100 ppm of $NaNO_2$ and 50 ppm of Zn^{2+} is shown in figure 2b. The NO_2^- stretching frequency of $NaNO_2$ shifted from 1268 to 1205.67

cm^{-1}. This confirms that the oxygen atom of the nitrite has coordinated with Fe^{2+} resulting in the formation Fe^{2+} - nitrite complex on the metal surface. Also there in possibility of anchoring of nitrite on the layer of consisting CaO, $Ca(OH)_2$,$CaCO_3$.

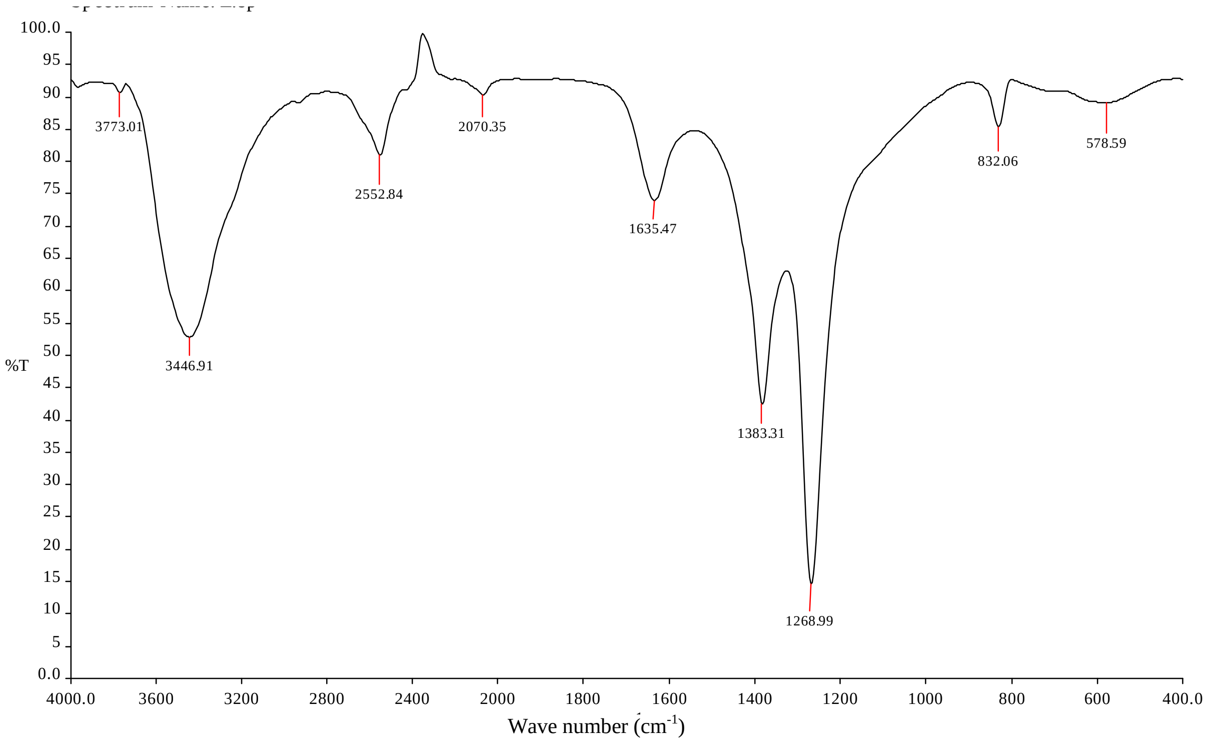

Fig.2a FTIR spectrum of pure sodium nitrite

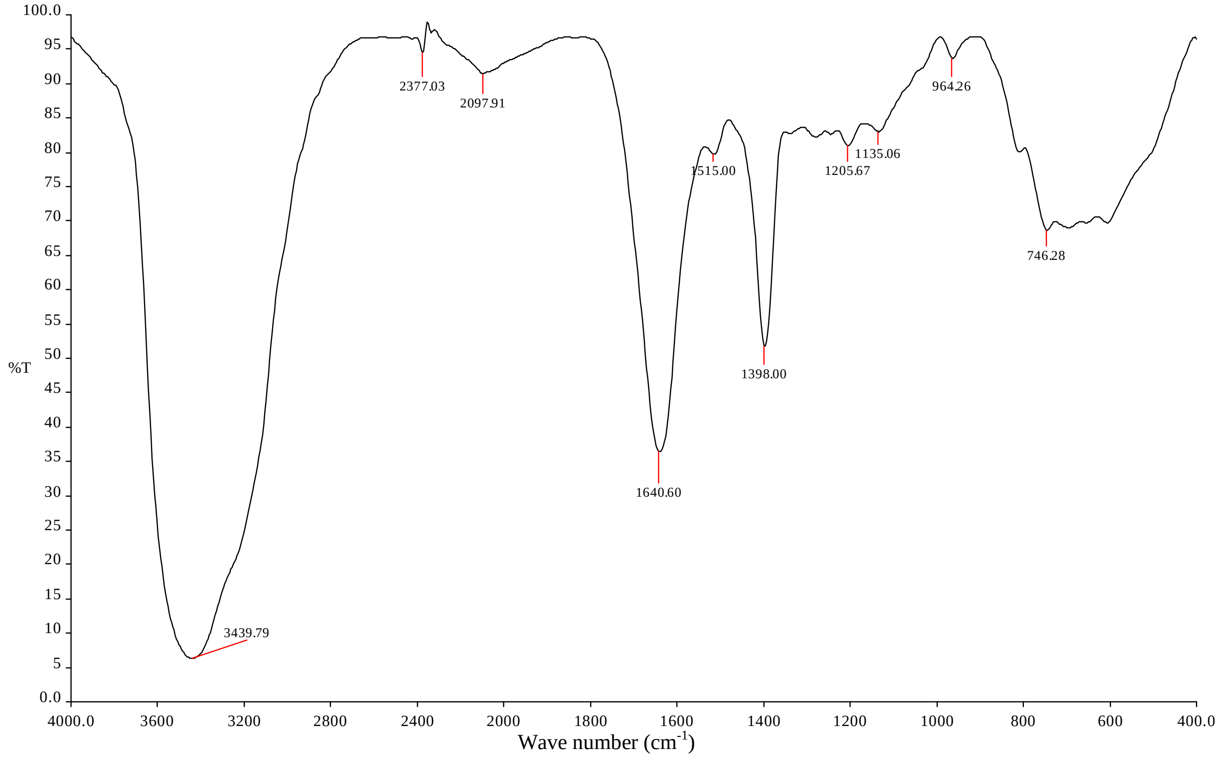

Fig.2b FTIR spectrum of film formed on the metal surface after immersion in aqueous solution containing SCPS+ 100 ppm SN+ 50 ppm of Zn^{2+}

Peak appears at 1398 cm^{-1} is due to Zn–O stretching. The - OH stretching frequency appears at 3439.79 cm$^{-1.}$ These observations indicate the presence of $Zn(OH)_2$ formed on the metal surface Peak appears at 1515, 746 and 1398 cm^{-}

[1]. These peaks confirm the presence of calcium carbonate, calcium oxide, calcium hydroxide and on the metal surface[7-8].

2. CYCLIC VOLTAMMETRY

Cyclic voltammograms have been used to investigate the corrosion behaviour of metals[9-12]. Deyab and Keera[9] have analysed the influence of sulphide, sulphate, and bicarbonate anions on the pitting corrosion behaviour of mild steel in formation water containing chloride ions by means of cyclic voltammetry technique. The cyclic voltammograms were recorded in the presence of increasing amounts (0.1 to 0.3M) of NaCl at a scan rate of 10 mV s^{-1}. The anodic response exhibits a well defined anodic peak followed by a passive region. The anodic peak is due to active metal dissolution and formation of ferrous hydroxide [13]. The cathodic sweep shows two cathodic peaks. The appearance of cathodic peak around -1.1 V is due to reduction of corrosion product, namely iron oxide to iron. The appearance of cathodic peak around -0.7 V is due to the reduction of pitting corrosion products precipitate on the electrode surface.

In the present study, cyclic voltammograms were recorded by measuring the working electrode, mild steel, in 3.5% NaCl solution. The cyclic voltammogram of mild steel immersed in 3.5% NaCl is shown in Fig 3a. It is observed that during anodic scan, no peak is observed but a passive state is noticed. This can be explained as follows: When the metal dissolves, ferrous hydroxide is formed. When the concentration of ferrous oxide at the anodic surface exceeds its solubility product, precipitation of solid oxide occurs on the electrode surface.

When the surface is entirely covered with oxide passive film, anodic current density does not increase indicating onset of passivation. In the passive state, the Cl^- ion can be adsorbed on the bare metal surface in competition with OH^- ions. As a result of high polarizability of the Cl^- ions, the Cl^- ions may adsorb preferentially [14]. The cathodic sweep shows only one peak at -0.652 V. This is due to the reduction of corrosion product, iron oxide to iron. The peak due to reduction of pitting corrosion product is absent. (This reveals that pitting corrosion does not take place under the given experimental conditions).

The cyclic voltammogram of mild steel, which has been immersed in SCPS for one day and dried is shown in Fig 3b. (brown iron oxide was observed on the mild steel electrode). It is observed that during anodic sweep, no peak appears, but a passive region is observed. During the cathodic sweep, the peak due to reduction of pitting corrosion product appears at -955 mV indicating that pitting corrosion takes place. However, the peak due to reduction of corrosion product, iron oxide, appears at -2.7 V. The current density increases from -2.5 $x10^{-3}$ A to-4.6 $x10^{-3}$ A. This indicates that when mild steel electrode is immersed in SCPS for one day, a protective film of iron oxide is formed on the electrode surface. It is stable in 3.5% NaCl solution. The increase in current density is explained as follows: Chloride ion is adsorbed on the passive film. The adsorbed chloride ion penetrates the oxide film especially at the flaws and defects in the oxide film [15].When the penetrated chloride ion reaches the metal surface, they promote local corrosion.

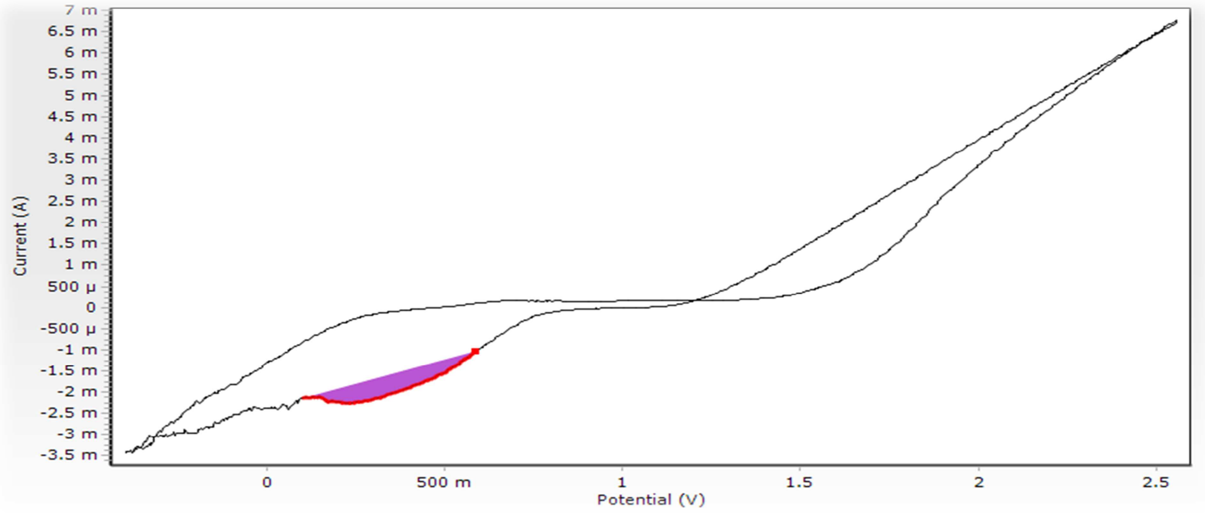

Figure 3a.Cyclic voltammogram of mild steel electrode immersed in 3.5% NaCl

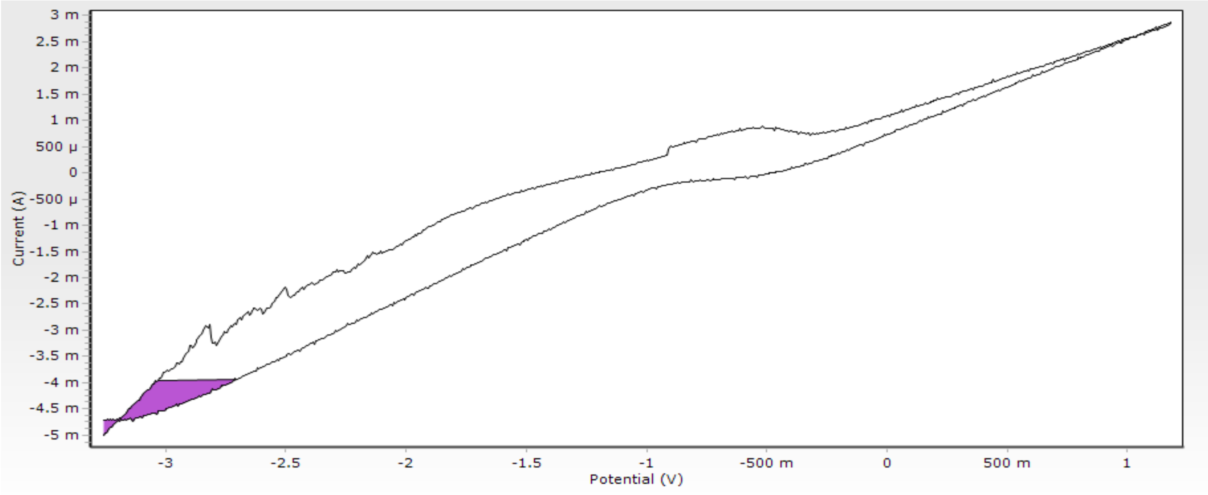

Figure.3b Cyclic voltammogram of mild steel electrode submerged in 3.5% NaCl solution after its immersion in SCPS for one day

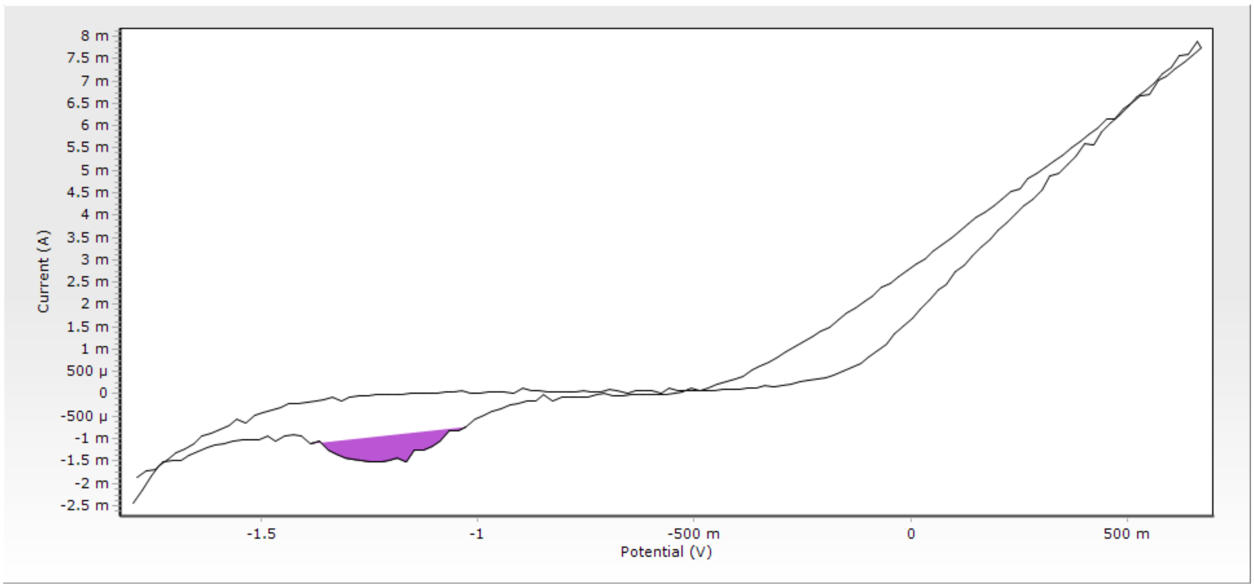

Figure.3c .Cyclic voltammogram of mild steel electrode submerged in 3.5% NaCl solution after its immersion in SCPS containing 100 ppm of SN and 50 ppm of Zn^{2+} for one day

When the mild steel electrode is immersed in SCPS water containing 100 ppm of SN and 50 ppm of Zn^{2+} for one day, a protective film is formed. It consists of Fe^{2+}– SN complex, Zn^{2+}– SN complex, and $Zn(OH)_2$ as revealed by FTIR spectroscopy. The cyclic voltammogram of mild steel electrode deposited with the above protective film is shown in Fig.3c. It is observed that during anodic sweep, dissolution of metal does not take place. This indicates that the protective film is stable and compact. Electrons are not transferred from the metal surface, and a passive region is observed. During cathodic sweep, the peak corresponding to reduction of pitting corrosion product appears at -850 mV. However, the peak due to reduction of iron oxide to iron appears at -1.31 V. The current density increases from -2.5×10^{-3} A to -1.5×10^{-3} A. The decrease in current density suggest that the adsorbed inhibitor molecule on the electrode surface not only effectively retard the anodic dissolution iron, but also enchanged the stability of ferrous species to be further oxiesed(Fe^{2+}) into ferric iron. It is observed from the Fig 2a, 2b, 2c that the pitting potentials for the three systems are at -656 mV, -970 mV, and -645 mV respectively. That is when mild steel electrode is immersed in the SCPS medium; the pitting potential is shifted to more negative side (active side, i.e., -970 mV). It accelerates corrosion because the protective film formed is porous and amorphous. When the electrode is immersed in the inhibitor medium, the pitting potential is shifted to the noble side, i.e., -645 mV. This indicates that the passive film found on the metal surface in the presence of inhibitors is compact and stable. It can withstand the attack of chloride ion present in 3.5 NaCl.

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