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A Study On Surface Analysis of shielding film formed on the Carbon metal by Tyrosine

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Abstract

A shielding film formed on the carbon metal surface by Tyrosine. It has been analysed by mass loss method, FTIR and Electrochemical method. From the mass loss method 250ppm of Tyrosine and 15ppm of Zinc gives 92% of inhibition efficiency. It reveals that the synergistic performance present among the Tyrosine and Zinc combination. The shielding film is analysed by FTIR spectroscopy method, from this study, Tyrosine- Zinc compound form a layer on the carbon metal surface and the electrochemical analysis such as cyclic volammetry confirmed the protective film formed on the carbon metal surface. The shielding film is stable at 3.5% of Nacl in cyclic volammetry analysis.

***Key words*: Aminoacid, Tyrosine, Zinc, FTIR, Carbon metal, cyclic volammetry**

INRODUCTION

Deterioration of metals is an electrochemical reaction that involves changes in mutually the metal and the environment in contact with the metal. While the mechanisms of deterioration are the same on a minute level, various microstructures, composition, and mechanical devise issues will lead to dissimilar manifestations of corrosion. Deterioration can have a variety of unconstructive effects on metal. When metal structures suffer from deterioration, they become unsafe which can lead to accidents, such as collapses. Even minor corrosion requires repairs and maintenance. While all metals corrode, it is estimated that 25-30% of corrosion could be prevented using suitable protection methods.

In the present study aminoacid is used as a deterioration inhibitor on the carbon metal surface. They are eco-friendly, nontoxic and easily available compounds. They contain two functional groups one is amino group and another one is carboxyl group. Both are act very good inhibitors on the carbon metal surface. The literature survey reveals that the aminoacids such as Glutamicacid, Tyrosine, Tryptophan, alanine, Cysteine, [1-7] are act as a good deterioration inhibitors.

In this study Tyrosine is used as corrosion inhibitors combined with Zinc compound. Basically Tyrosine is a good inhibition character, because it has amino group and delocalized bi electrons and its act as a shielding layer on the metal surface. It also contain hydroxyl group combined with benzene atom also enhanced their inhibition actions.

The present work investigates shielding film formed on the carbon metal surface by mass loss method, FTIR and Electrochemical studies.

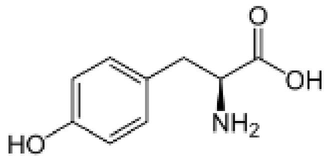
Material and methods

Mass loss method

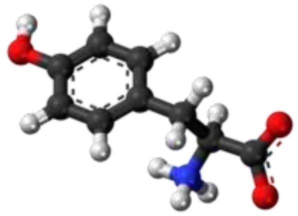
Carbon metal specimens were immersed in 100 mL of the sea water containing various concentrations of the Tyrosine in the presence and absence of Zinc for one day. The weight of the specimens before and after immersion was determined using a Shimadzu balance, model AY62. The corrosion products were cleansed with Clarke's solution17. The inhibition efficiency (IE) was then calculated using the equation:

$IE = 100 [1- (w2 / w1)] \%$

Where w1 = corrosion rate in the absence of the inhibitor, w2 = corrosion rate in the presence of the inhibitor. 2D & 3D Structures of Tyrosine,



2D



3D

Surface examination study

The carbon metal specimens were immersed in various test solutions for a period of 1 day. After 1 day, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimen was analyzed by a surface analysis technique

Surfaces analysis by FTIR spectra

FTIR spectra give specific information about chemical bonding and molecular structures, making it useful for analyzing organic molecules and some inorganic materials. Chemical bonds vibrate at characteristic frequencies and when exposed to infrared radiation, they absorb the radiation at frequencies that match their vibration modes. Measuring the radiation absorption as a function of frequency produces that can be used to identify functional groups and compounds.

In the present analysis after the immersion period of one day in various environments, the specimens were taken out of the test solution and tried. The film formed on the surface was scratched carefully using a period glass rod and was thoroughly mixed with KBr so as to make it uniform throughout. FTIR spectrum of the powder (KBr) pellet was recorded in a Perkin-Elmer-1600 spectrophotometer with a resolving power of 4 cm^{-1}.

Cyclic Voltammetry

Cyclic voltammetry is a type of potentiodyamic electrochemical measurements. This technique has been employed for understanding kinetic parameters for the electrode reaction mechanism for both organic molecules as well as ions. CV system consists of an electrolysis cell, a potentiostat, a current- to –voltage converter and a data acquisition system. The electrolysis cell consists of a working electrode, counter electrode, reference electrode and electrolytic solution. The working electrode, counter electrode's potential is varied linearly with time, while the reference electrode maintains a constant potential. The counter electrode conducts electricity solution is to provide ions to the electrodes during oxidation and reduction. A potentiostat is an electronic device which uses a DC power source to produce a potential, which can be maintained and accurately determined, while allowing small currents to be drawn into the system without changing the voltage. The current- to –voltage converter measures the resulting current and the data acquisition system produce the resulting voltammogram.

In the present study, cyclic voltammograms were recorded in VersaSTAT MC electrochemical system. A three-electrode cell assembly was used with electrolytic solution. The working electrode was carbon steel. The exposed surface area was 1 cm^2. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode was immersed in sea water in the presence and absence of inhibitor for a period of one day. After one day, the carbon steel electrodes were taken out and dried. The nature of the film formed on the electrode surface was immersed in 3.5% NaCl solution. From the cyclic voltammetry study, electrochemical parameters such as peak potential, current density and the pitting potential were calculated. The cyclic voltammetry curves were recorded in the scan range of −1.8 to −1.8 V (SCE) with a scan rate of 20 mV s^{-1}.

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RESULTS AND DISCUSSION

Analysis of Weight loss Study

The calculated deterioration inhibition efficiency (IE) of Tyrosine in scheming deterioration of carbon metal in sea water, for a period of one day in absence and presence of Zinc ($Zn^{2+)}$ are given in Table.1

It is observed from the Table. 1 the calculated value indicates the ability of Tyrosine to be a good inhibitor. The IE is found to be improved in the presence of Zn^{2+}. Tyrosine alone has some inhibition efficiencies. 50 ppm of Tyrosine shows 23% of IE, as the concentration of Tyrosine increases, the IE also increases. Correspondingly for a given concentration of Tyrosine, the IE increases as the concentration of Zn^{2+} increases. A synergistic effect exists between Tyrosine and Zn^{2+}. For example, 15 ppm of Zn^{2+} has 41 % of IE; 250 ppm of Tyrosine has 56 % of IE. Interestingly their combination has high IE, namely, 92%. Therefore the mixture of inhibitors shows better IE than as individual inhibitors. In the presence of Zn^{2+}, more amount of Tyrosine is transported towards the metal surface. This accounts for the synergistic effect existing between Zn^{2+} and Tyrosine. [4, 8-12]

Table. 1.Inhibition efficiencies (IE) of Tyrosine - Zn^{2+} systems, when the carbon metal immersed in sea water

Tyrosine (ppm)	Zn^{2+} (0 ppm)	Zn^{2+} (15 ppm)
	IE %	IE%
0	-	41
50	23	44
100	26	54
150	32	58
200	42	78
250	56	92

Analysis of FTIR spectra

FTIR spectrum of pure Tyrosine is given in Fig. 1a. The CN stretching frequency appears at 1160 cm^{-1}. The C=O stretching frequency of carboxyl group appears at 1598 cm^{-1}.The NH stretching frequency appears at 3432 cm^{-1} .The FTIR spectrum of the film formed on the metal surface after immersion in the sea water for 1 day containing 250 ppm of Tyrosine and 15 ppm of Zn^{2+} is shown in Fig.1b. From the CN stretching frequency has shifted from 1160 cm^{-1} to 1062 cm^{-1}. The C=O stretching frequency shifted from 1689 cm^{-1} to 1630 cm^{-1}. The NH stretching frequency shifted from 3432 cm^{-1} to 3205 cm^{-1}. This indicates that the nitrogen atom of Tyrosine coordinated with Fe^{2+} is formed on the metal surface, resulting in the formation of Fe^{2+}- Tyrosine complex on the anodic sites of the metal surface. The peak at 1396 cm^{-1} is due to Zn-O stretching. The stretching frequency due to –OH appears at 3123 cm^{-1}. Thus FITR analysis leads to the conclusion that the protective film consist of Fe^{2+} - Tyrosine complex and $Zn(OH)_2$ on the metal surface.[13-14]

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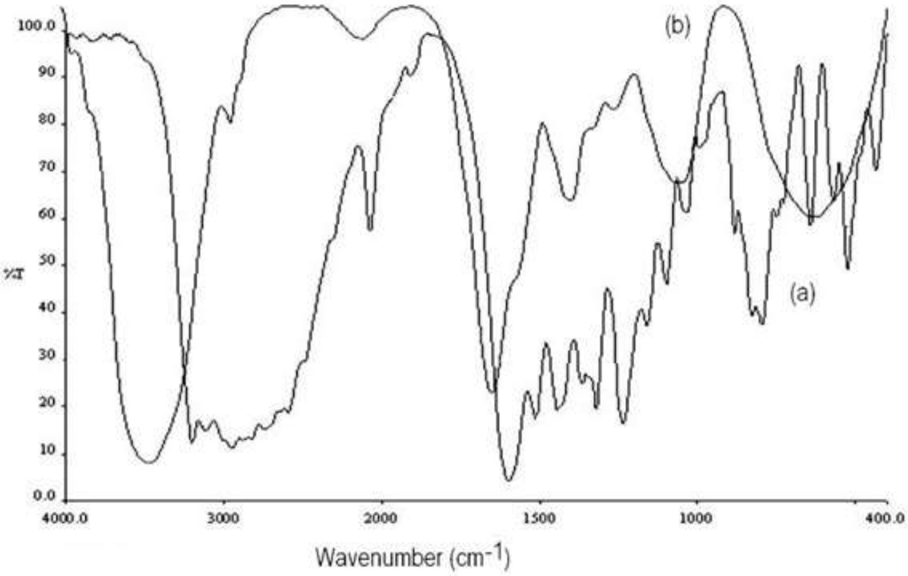

Fig1a &1b. FTIR spectra

a) Pure Tyrosine

b)Film formed on the metal surface after immersion in the sea water for 1 day containing 250 ppm of Tyrosine and 15 ppm of Zn^{2+}

Cyclic voltammetry

In this study cyclic voltammograms were recorded by immersing the working electrode, carbon metal, 3.5% NaCl solution. The cyclic voltammogram of carbon metal immersed in 3.5% NaCl is shown in Fig.2. It is observed that during anodic scan no peak was observed rather passive state is observed. 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 oxide occurs on the electrode surface. When the surface is entirely covered with oxide passive film anodic current density does not increases representing onset of passivation. In the passive state, the Cl^- ion can be adsorbed on the base metal surface in competition with OH^- ions. As a result of high polarizability of the Cl^- ions, the Cl^- ions may adsorb. The cyclic voltammetry parameters are given in Table From the Table.2 cathodic sweeps shows only one peak at -1.12V. This is due to the reduction of corrosion product iron oxide to iron. The peak is due to the absence of reduction of pitting corrosion product. (This reveals that pitting corrosion does not take place under the given experimental conditions).

The cyclic voltammogram of carbon metal, which has been immersed in sea water for one day and dried, is shown in Fig.3. (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 is due to the reduction of pitting corrosion product which appears at -528, indicating that pitting corrosion takes place. However, the peak due to reduction of corrosion product, iron oxide, appears at -1.133V. The current density increases from -1.148 $x10^{-3}$ A to -1.172 $x10^{-3}$ A. This indicates that when mild steel electrode is immersed in sea water for one day, a protective film of iron oxide is formed on the electrode surface. It is stable in 3.5% NaCl solution. The increases in the current density are explained as follows. Chloride ion is adsorbed on the passive film. The absorbed chloride ion penetrates the oxide film especially at the flaws and defects in the oxide film. When the penetrated chloride ion reaches the metal surface they promote local corrosion.

When the mild steel electrode is immersed in sea water containing 250 ppm of Tyrosine and 15 ppm of Zn^{2+} for one day, a protective film is formed. It consists of Fe^{2+}- Tyrosine complex, Zn^{2+} - Tyrosine complex and $Zn(OH)_2$, as revealed by FTIR spectroscopy. The cyclic voltammogram of carbon steel electrode, deposited with the above protective film, is shown in Fig.4. It is observed that during anodic sweep, dissolution of metal does not take place. This indicates that the protective

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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 -460 mV. However, the peak due to reduction of iron oxide to iron appears at -1.333 V. The current density increases from -1.148 x10^{-3} A to -2.264 x10^{-3} A. The increase in current density may be explained as above. It is observed from the Fig.3, 4 & 5 that the pitting potentials for the three systems are at -644.4 mV, -755.5 mV, and -560 mV respectively. That is when carbon metal electrode is immersed in the sea water medium; the pitting potential is shifted to more negative side (active side, i.e., -755.5 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., -560 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. [15-16]

Table.2 Cyclic voltammetry parameters (Tyrosine+ Zn^{2+})

Sample	Ep (V)	Peak ip (A)	Pitting corrosion product (mV)	Pitting potential (mV)
Control (Carbon metal)	-1.12	-1.148× 10^{-3}	-	-644.4
Blank (sea water)	-1.133	-1.172× 10^{-3}	-528	-755.5
Inhibitor system (Tyrosine+ Zn^{2+})	-1.333	-2.264 × 10^{-3}	-460	-560

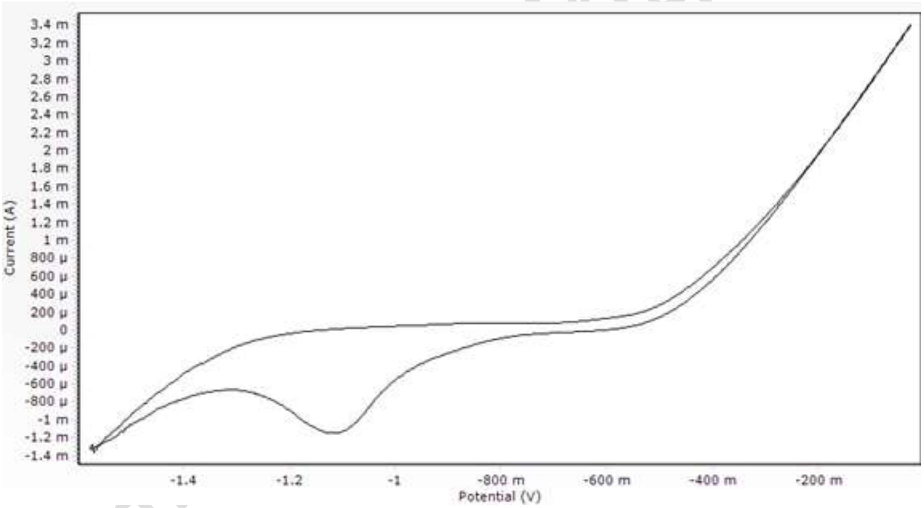

Fig. 3. Cyclic voltammogram of carbon steel immersed in 3.5% NaC

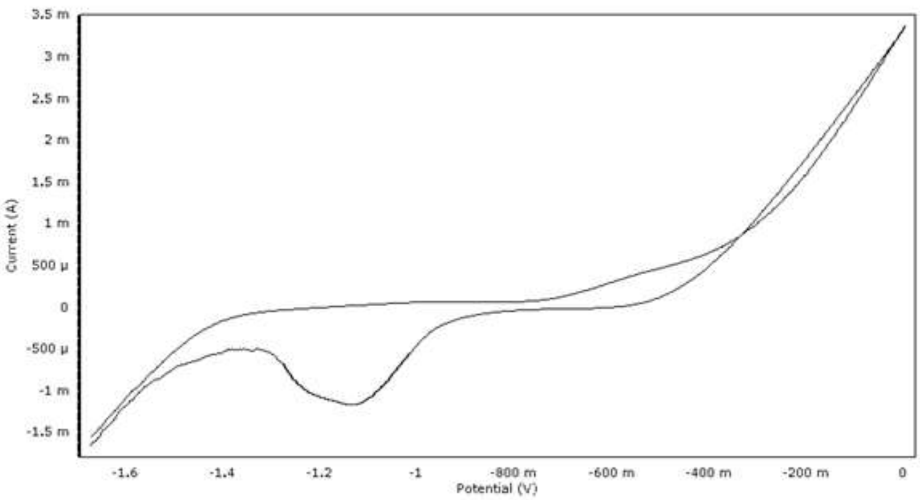

Fig.4. Cyclic voltammogram of carbon metal immersed in sea water for one day

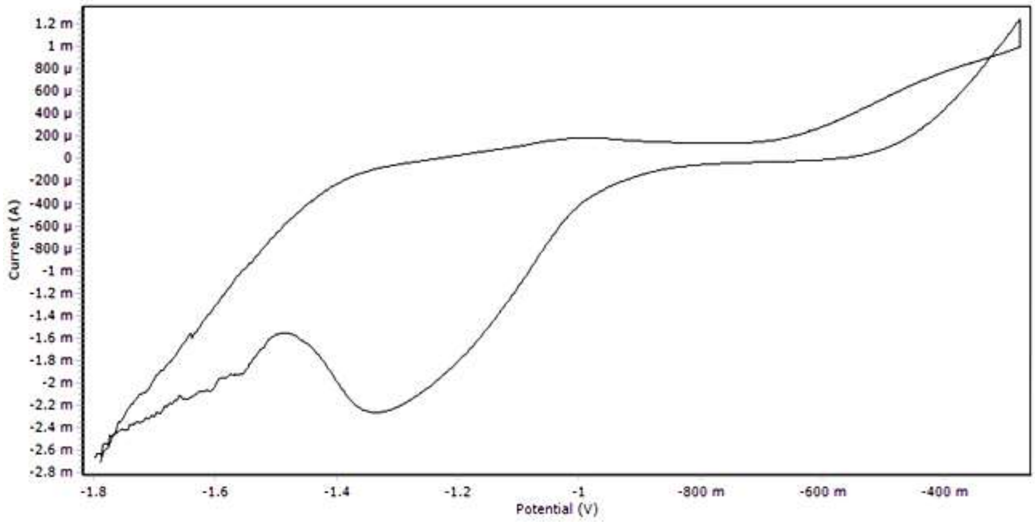

Fig.5. Cyclic voltammogram of carbon metal electrode, deposited with protective film

Conclusion

- A shielding film formed on the carbon metal surface by Tyrosine, it has been analysed by mass loss method, FTIR and Electrochemical method.
- From the mass loss method 250ppm of Tyrosine and 15ppm of Zinc gives 92% of inhibition efficiency.
- It reveals that the synergistic behaviour present between the Tyrosine and Zinc combination.
- The shielding film is analysed by FTIR spectroscopy method, from this study, Tyrosine- Zinc compound form a layer on the carbon metal surface
- The electrochemical analysis such as cyclic volammetry confirmed the protective film formed on the carbon metal surface. The protective film is stable at 3.5% of Nacl in cyclic volammetry analysis.

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