



CYCLIC VOLTAMMETRIC STUDY OF PROTECTIVE FILM FORMED BY 2-CARBOXYETHYLPHOSPHONIC ACID - Ni²⁺ SYSTEM ON CARBON STEEL

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The corrosion inhibition effect of carbon steel in sea water by 2-carboxyethylphosphonic acid (2-CEPA) and Ni²⁺ has been investigated using weight loss method and cyclic voltammetry. The results show that 73% inhibition efficiency is achieved with binary system consisting of 250 ppm of 2-CEPA and 50 ppm of Ni²⁺. 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 Fe²⁺ – 2-CEPA complex, Ni²⁺ – 2-CEPA complex and Ni(OH)₂. Cyclic voltammetry study reveals that the protective film is more compact and stable even in 3.5% NaCl environment.

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INTRODUCTION

The corrosion in sea water is severe due to the presence of chloride ions and dissolved oxygen. Corrosion can cause great damages to marine steel infrastructures such as bridges, wharfs, platforms, and pipeline systems. It has been estimated that some 20% of the corrosion cost is due to microbial corrosion and degradation.¹ Metals obtain stability when their surfaces are separated from the normal terrestrial environment.² If this isolation is not achieved, they undergo a process of embrittlement, suffer fatigue, and transform into oxides, which peel off or just dissolve away. Metals become unstable when they contact moist atmosphere containing carbon-dioxide or sodium chloride suspension in marine atmosphere. The spontaneous corrosion of metal or its alloys results from the charged transfer reactions at their interface between the metal and its electrolytic environment.^{3,4} The goal of studying the processes of corrosion is to find methods of minimizing or preventing it. Inhibition of corrosion and scaling can be done by the application of inhibitors. Most of the organic inhibitors containing nitrogen, oxygen, sulfur atoms, and multiple bonds in their molecules facilitate adsorption on the metal surface.^{5,6} Several phosphonic acids have been used as corrosion inhibitor.⁷⁻¹¹ Phosphonic acids are organic compounds containing R-PO(OH)₂ or R-PO(OR)₂ groups. They are effective chelating agents that are used in cooling water and desalination systems to inhibit scale formation and corrosion. Phosphonic acids are extensively used now-a-days due to their complex forming abilities, high stability under harsh conditions, and low toxicity.^{12,13} The inhibition efficiency of phosphonates depends on the number of phosphono groups in a molecule and also on different substituents. Compounds with a phosphonic functional group are considered to be the most effective chemical for inhibiting

the corrosion process and it is well known that short-chain-substituted phosphonic acids are good corrosion inhibitors for iron and low-alloyed steels.¹⁴

An environmental friendly compound, 2-carboxyethylphosphonic acid, contains not only phosphono groups, but also carboxyl and ethyl groups, which can decrease corrosion. The present study aims **a**) to find out the corrosion inhibition effects of 2-CEPA and Ni²⁺ system on carbon steel in sea water medium using weight-loss method; their inhibitive action is due to coordination of the oxygen atom of the carboxylate anion to the metal ions to form metal-inhibitor complexes **b**) electrochemical techniques provide information on the corrosion rate, as well as on processes at interfaces affected by additives **c**) to analyze the protective film by Fourier Transform Infrared Spectroscopy (FTIR) **d**) to propose a suitable mechanism of corrosion inhibition based on the results from the above studies.

EXPERIMENTAL

Preparation of Specimen

Carbon steel specimen [0.0267 % S, 0.06 % P, 0.4 % Mn, 0.1 % C and the rest iron] of dimensions 1.0 cm x 4.0 cm x 0.2 cm were polished to a mirror finish and degreased with trichloroethylene.

Weight-Loss Method

Carbon steel specimens in triplicate were immersed in 100 mL of the solutions containing various concentrations of the inhibitor in the presence and absence of Ni²⁺ (as NiSO₄ · 6H₂O) for one day. The weight of the specimens before and after immersion was determined using a Shimadzu balance, model AY62. The corrosion products were cleaned with Clarke's solution.¹⁵ The inhibition efficiency (IE, %) was then calculated using the equation:

$$IE = 100 \left[1 - \frac{W_2}{W_1} \right] \quad (1)$$

where W_1 is the weight loss value in the absence of inhibitor and W_2 is the weight loss value in the presence of inhibitor.

Cyclic Voltammetry

Cyclic voltammograms were recorded in VersaSTAT MC electrochemical system. A three-electrode cell assembly was used. The working electrode was carbon steel. The exposed surface area was 1 cm². A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode. 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.

Fourier Transform Infrared Spectra (FTIR)

The FTIR spectra were recorded in a Perkin-Elmer-1600 spectrophotometer. The film formed on the metal surface was carefully removed and mixed thoroughly with KBr making the pellet.

RESULTS AND DISCUSSION

Weight-Loss Method

The physicochemical parameters of sea water are given in Table 1. Table 2 gives values of the corrosion inhibition efficiencies and the corresponding corrosion rates of 2-carboxyethyl phosphonic acid (2-CEPA) – Ni²⁺ in controlling corrosion of carbon steel in sea water for a period of 24 hours at room temperature. The 2-CEPA alone has high rate of corrosion. The inhibition efficiency of 2-CEPA is improved by adding various concentrations of Ni²⁺. Similar observations have been made by Abdallah et al.,¹⁶ who studied the inhibiting effect of 3-methylpyrazolone with Ni²⁺ cation for carbon steel in sulfuric acid solution. However, increasing the concentration of 2-CEPA as well as Ni²⁺, the maximum inhibition is achieved and the corrosion rate is decreased. It is found that 250 ppm of 2-CEPA and 50 ppm of Ni²⁺ has 73% inhibition efficiency. The inhibition efficiency increases with the increase of concentration of inhibitors. This behavior could be attributed to the increase of the surface area covered by the adsorbed molecules of phosphonic acid with the increase of its concentration. It is generally assumed that the adsorption of the inhibitor at the metal/solution interface is the first step in the mechanism of inhibition in aggressive media.

Cyclic Voltammetry

Cyclic voltammograms have been used to investigate the corrosion behaviour of metals.¹⁷⁻²⁰ Deyab and Keera²⁰ have analysed the influence of sulphide, sulphate, and bicarbonate anions on the pitting corrosion behaviour of carbon 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 0.3 M) 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.²¹ 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.

Table 1. The physicochemical parameters of natural sea water collected in Mandapam, Tamilnadu, India.

Parameter	Value
Total dissolved salts (mg L ⁻¹)	78136
Electrical conductivity (μΩ ⁻¹ cm ⁻¹)	70788
pH	7.82
Total Hardness (CaCO ₃ equivalent)	24500
Calcium as Ca ²⁺ (mg L ⁻¹)	2200
Magnesium as Mg ²⁺ (mg L ⁻¹)	1800
Sodium as Na ⁺ (mg L ⁻¹)	9600
Chloride as Cl ⁻ (mg L ⁻¹)	23100
Fluoride as F ⁻ (mg L ⁻¹)	1.2
Potassium (mg L ⁻¹)	900
Sulphate as SO ₄ ²⁻ (mg L ⁻¹)	2350

In the present study, cyclic voltammograms were recorded by measuring the working electrode, carbon steel, in 3.5% NaCl solution. The cyclic voltammogram of carbon steel immersed in 3.5% NaCl is shown in Fig.1a. 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.²⁰ 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.²²

The cathodic sweep shows only one peak at -1.12 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.

The cyclic voltammogram of carbon steel, which has been immersed in sea water for one day and dried is shown in Fig.1b. (brown iron oxide is observed on the carbon 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 -528 mV indicating that pitting corrosion takes place. However, the peak due to reduction of corrosion product, iron oxide, appears at -1.133 V. The current density increases from -1.148 x 10⁻³ A to -1.172 x 10⁻³ A.

Table 2. The inhibition efficiency (IE%) and the corrosion rate (mm y⁻¹) of 2-CEPA – Ni²⁺ system are determined by weight-loss method.

2-CEPA, ppm	Ni ²⁺ (ppm)					
	0		25		50	
	IE, %	CR, mm y ⁻¹	IE, %	CR, mm y ⁻¹	IE, %	CR, mm y ⁻¹
0	-	0.1858	8	0.1709	15	0.1579
50	15	0.1579	22	0.1449	51	0.0910
100	21	0.1468	28	0.1338	60	0.0743
150	26	0.1375	33	0.1245	65	0.0650
200	30	0.1301	39	0.1133	69	0.0576
250	35	0.1208	44	0.1040	73	0.0501

This indicates that when carbon 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 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.²³ When the penetrated chloride ion reaches the metal surface, they promote local corrosion.

When the carbon steel electrode is immersed in sea water containing 250 ppm of 2-CEPA and 50 ppm of Ni²⁺ for one day, a protective film is formed. It consists of Fe²⁺- 2-CEPA complex, Ni²⁺- 2-CEPA complex, and Ni(OH)₂ as revealed by FTIR spectroscopy. The cyclic voltammogram of carbon steel electrode deposited with the above protective film is shown in Fig.1c. 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 -500 mV. However, the peak due to reduction of iron oxide to iron appears at -1.476 V. The current density increases from -1.148 x10⁻³ A to -3.388 x10⁻³ A. The increase in current density may be explained as above. It is observed from the Fig.1a, 1b, 1c that the pitting potentials for the three systems are at -644.4 mV, -755.5 mV, and -606.3 mV respectively. That is when carbon steel 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., -606.3 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.

FTIR Spectra

FTIR spectra have been used to analyze the protective film found on the metal surface.^{24,25} The FTIR spectrum (KBr) of pure 2-CEPA is shown in Fig. 2a. The P-O stretching frequency appears at 1017 cm⁻¹ and the C=O stretching frequency of the carboxyl group appears at 1721 cm⁻¹. The FTIR spectrum of the film formed on the metal surface after immersion in sea water containing 250 ppm of 2-CEPA and 50 ppm of Ni²⁺ is shown in Fig. 2b.

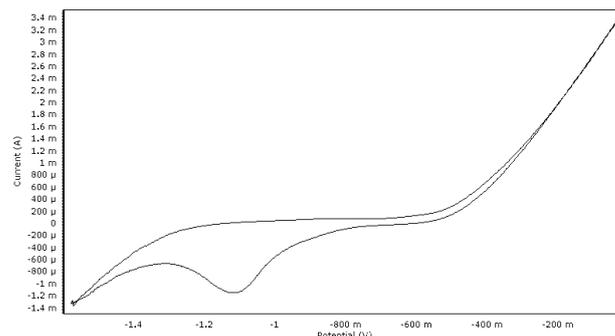


Figure 1a. Cyclic voltammogram of carbon steel electrode immersed in 3.5% NaCl.

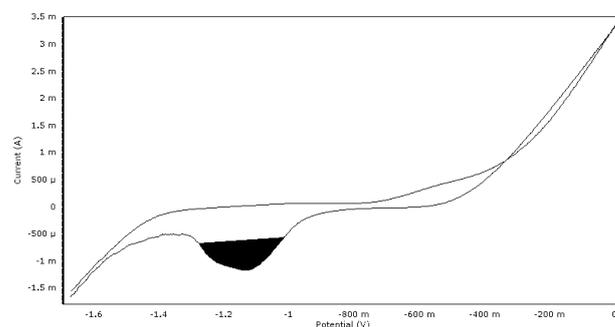


Figure 1b. Cyclic voltammogram of carbon steel electrode submerged in 3.5% NaCl solution after its immersion in sea water for one day.

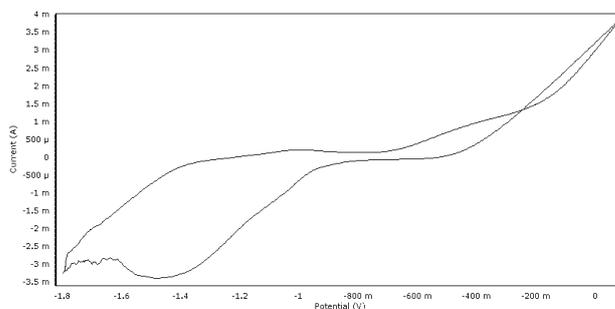


Figure 1c. Cyclic voltammogram of carbon steel electrode submerged in 3.5% NaCl solution after its immersion in sea water containing 250 ppm of 2-CEPA and 50 ppm of Ni²⁺ for one day.

The P-O stretching frequency has shifted from 1017 to 1090 cm⁻¹ and the C=O stretching frequency has shifted from 1721 to 1701 cm⁻¹. It is inferred that oxygen atom of the carboxyl group has coordinated with Fe²⁺ resulting in the formation of Fe²⁺ – 2-CEPA complex formed on the anodic sites of the metal surface. The possibility of formation of Ni²⁺ – 2-CEPA complex, to some extent, on the metal surface cannot be ruled out. The peak at 3432 cm⁻¹ is due to –OH stretching. The band due to Ni-O appears at 1369 cm⁻¹. These results confirm the presence of Ni(OH)₂ deposited on the cathodic sites of the metal surface. Thus, FTIR spectral study leads to the conclusion that the protective film consists of Fe²⁺ – 2-CEPA complex, Ni²⁺ – 2-CEPA complex and Ni(OH)₂.

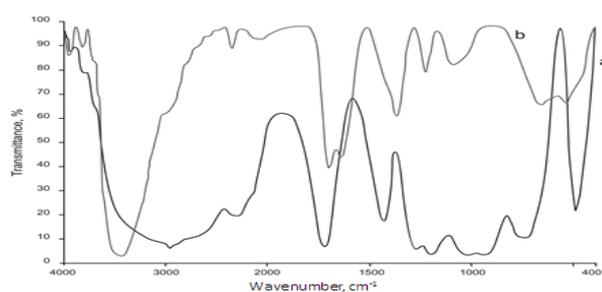


Figure 2. FTIR Spectra a) pure 2-CEPA b) film formed on metal surface after immersion in sea water containing 250 ppm of 2-CEPA and 50 ppm of Ni²⁺

Mechanism of Corrosion Inhibition

In order to explain the above results, the following mechanism of corrosion inhibition is proposed: When carbon steel is immersed in an aqueous solution, the anodic reaction is,



The corresponding cathodic reaction is reduction of oxygen to hydroxyl ions,



When the formulation consists of 250 ppm of 2-CEPA and 50 ppm Ni²⁺ in sea water, there is formation of 2-CEPA – Ni²⁺ complex in solution.

When carbon steel is immersed in this environment, the 2-CEPA – Ni²⁺ complex diffuses from the bulk of the solution to the metal surface. The 2-CEPA – Ni²⁺ complex is converted into 2-CEPA – Fe²⁺ complex on the anodic sites of the metal surface, the stability of Fe²⁺ – 2-CEPA complex is higher than the corresponding Ni complex.



The released Ni²⁺ combines with OH⁻ to form Ni(OH)₂ on the cathodic sites of the metal surface.



The possibility of formation of Ni²⁺ – 2-CEPA complex, to some extent, on the metal surface cannot be ruled out.

Thus, the protective film consists of Fe²⁺ – 2-CEPA complex, Ni²⁺ – 2-CEPA complex, and Ni(OH)₂.

CONCLUSIONS

The conclusions drawn from the results may be given

(1) The inhibition of corrosion of carbon steel in sea water has been evaluated in the absence and presence of 2-carboxyethylphosphonic acid and Ni²⁺.

(2) Weight-loss method and cyclic voltammetry have been used for this purpose.

(3) The formulation consisting of 250 ppm of 2-CEPA and 50 ppm of Ni²⁺ provides 73% inhibition efficiency.

(4) FTIR study reveals the protective film consists of Fe²⁺ – 2-CEPA complex, Ni²⁺ – 2-CEPA complex, and Ni(OH)₂.

(5) Cyclic voltammetry study reveals that the protective film is more compact and stable even in 3.5% NaCl environment.

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