# Corrosion Inhibition of Carbon steel by Succinic acid – $Zn^{2+}$ system

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## Abstract

*The inhibition efficiency (IE) of succinic acid (SA) in controlling corrosion of carbon steel in sea water in the absence and presence of $Zn^{2+}$ has been evaluated by weight loss method. The formulation consisting of 250 ppm SA and 50 ppm $Zn^{2+}$ has 93% IE. It is found that the inhibition efficiency (IE) of SA increases by the addition of $Zn^{2+}$ ion. A synergistic effect exists between SA and $Zn^{2+}$. Polarization study reveals that SA – $Zn^{2+}$ system controls the cathodic reaction predominantly. FTIR spectra reveal that the protective film consists of $Fe^{2+}$ – SA complex and $Zn(OH)_2$. The surface morphology of the protective film on the metal surface was characterized by scanning electron microscopy (SEM) study. A suitable mechanism for corrosion inhibition is proposed based on the results from the above studies.*

**Keywords:** Corrosion inhibition, succinic acid, carbon steel, synergistic effect, sea water.

## Introduction

Corrosion is a natural phenomenon that cannot be avoided completely, but it can be controlled and prevented. It means corrosion mitigation and control methods shall be properly selected to meet the specific environment and operational condition. Based on the metal/environment combinations, different types of inhibitors are used in suitable concentrations. The use of inhibitors is an important method of protecting materials against deterioration from corrosion[1-3]. Several carboxylates such as sodium salicylate[4], sodium cinnamates[5], anthranilate[6] and adipate[7] have been used as inhibitors. These inhibitors are described by the formula $R(COO^-)_n$, where R can be alkyl or aryl and n is usually 1 or 2 but can be 3 to 6. A very wide range of such chemicals have been shown to be effective inhibitors of the corrosion of mild steel. The chief requirement seems to be that the R – COOH acid should have $pK_a$ value of atleast 4. Thus, in straight chain mono carboxylic acids the sodium salt of formic acid H – COOH with $pK_a$ = 3.75 is not inhibitive whereas the higher members of the series, beginning with acetate, $pK_a$ = 4.76 are inhibitive. Similarly, with the dicarboxylicates $(CH_2)_n (COO^-)_2$ oxalate with n = 0 and $pK_a$ = 1.23 and malonate with n = 1 and $pK_a$ = 2.54 are non inhibitive where as higher members of the series i.e. succinate ($pK_a$ = 4.17), azelate ($pK_a$ = 4.54) and sebacate ($pK_a$ = 4.55) are very good inhibitors[4]. It has also been shown[4] that for aryl carboxylates ortho–substituted benzoate are less effective than meta–or para– substituted compounds. This effect is also presumably associated with the lower $pK_a$ values of ortho compounds since there is a little difference in efficiency between ortho and para substituted cinnamates for which the $pK_a$ values are similar.

This observation on the acid strength is probably the only reliable statement that can be made in predicting whether a carboxylate will be an inhibitor and even this prediction may relate only mild steel. The inhibitive properties of carboxylates to other metals and alloys are, so far, impossible to predict. Benzoates is good inhibitor of corrosion of mild steel but not of cast iron or $Zn^4$ whereas structurally relates cinnamate is effective for these other metals.

A ring structure for the inhibitor molecules is not essential for the protection of cast iron since some aliphatic dicarboxylates have this property[5]. Generally the substituted cinnamates are better than substituted benxoates as inhibitors. Experience with benzoates suggests that carboxylates are 'safe' inhibitors in the sense that they are less likely to promote localized attack than some other anodic inhibitors in the presence of excess chloride or sulphate. Further work is needed to confirm this property with other carboxylates. Reviews of carboxylates as corrosion inhibitors have appeared from time to time[4, 6-10]. More detailed studies of particular carboxylates have also been published[11-16]. Corrosion of tin in citric acid solution and effect of some inorganic anion have been studied[17]. Synergistic effect of SA and $Zn^{2+}$ in controlling corrosion of carbon steel in well water has been reported[18]. The corrosion inhibition of carbon steel by sodium potassium tartrate has been studied by Arockia selvi et al.[19]. Florence et al.[20] have investigated the corrosion inhibition of carbon steel by adipic acid. The inhibition efficiency of sodium potassium tartrate in controlling corrosion of stainless steel in sea water has been studied by Wilson et al.[21]. The SA is a dicarboxylic acid and the two oxygen atoms in the carboxyl groups have ability to

coordinate with metal ions due to their lone pairs of electrons and it can act as an inhibitor[22] figure 1. The aim of the present study was to investigate synergistic corrosion inhibition for the SA and $Zn^{2+}$ combination to carbon steel in marine sample collected from Bay of Bengal at Marina beach which is located at Chennai, Tamil Nadu, India table 1. The corrosion inhibition efficiency was calculated using weight loss method and polarization study. The protective film formed on the metal surface characterized using surface morphological studies such as Fourier Transform Infrared spectra (FTIR) and scanning electron microscopy (SEM) study.
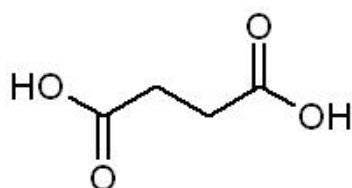
**Figure-1**
**Structure of succinic acid**

## Material and Methods

**Preparation of the specimens:** Carbon steel specimen (0.026% S, 0.06% P, 0.4% Mn and 0.1% C and rest iron) of the dimensions 1.0 X 4.0 X 0.2 cm were polished to a mirror finish and degreased with trichloroethylene and used for the weight-loss method and surface examination studies.

**Weight – Loss Method:** Carbon steel specimens in triplicate were immersed in 100 mL of the sea water containing various concentrations of the inhibitor in the presence and absence of $Zn^{2+}$ for three days at $25 \pm 0.1^{\circ}$C. The corrosion product cleaned with Clark's solution[23]. The parameter of the sea water is given in table 1.

**Table-1**
**Physico – Chemical Parameters of sea water**

| Parameters | Value | |
|---|---|---|
| pH | 7.66 | |
| Conductivity | 44200 | µmhos/cm |
| Chloride | 16050 | ppm |
| Sulphate | 2616 | ppm |
| TDS | 30940 | ppm |
| Total hardness | 2800 | ppm |
| Calcium | 120 | ppm |
| Sodium | 6300 | ppm |
| Magnesium | 600 | ppm |
| Potassium | 400 | ppm |

The weights of the specimens before and after immersion were determined using a balance, Shimadzu AY62 model.

Then the inhibition efficiency was calculated using the equation (1)

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

Where $W_1$ and $W_2$ are Corrosion rate in the absence and presence of inhibitor respectively.

The corrosion rate (CR) was calculated using the formula

$$CR = \frac{87.6\,W}{DAT}\ mm/y$$

Where, W = weight loss in mg, D = 7.87 $g/cm^3$, A = surface are of the specimen (10 $cm^2$) and T = 72 hrs.

**Potentiodynamic Polarization study:** Polarization study was carried out in Electrochemical Impedance Analyzer model CHI 660A using a three electrode cell assembly. The working electrode was used as a rectangular specimen of carbon steel with one face of the electrode of constant 1 $cm^2$ area exposed. A saturated calomel electrode (SCE) was used as reference electrode. A rectangular platinum foil was used as the counter electrodes. Polarization curves were recorded after doing iR compensation. The corrosion parametrs such as Tafel slopes (anodic slope $b_a$ and cathodic slope $b_c$), corrosion current ($I_{Corr}$) and corrosion potential ($E_{Corr}$) values were calculated. During the polarization study, the scan rate (V/s) was 0.005; Hold time at Ef (s) was zero and quiet time (s) was 2.

**Surface Examination Study:** The carbon steel specimens were immersed in various test solutions for a period of one day. After one day the specimens were taken out and dried. The nature of the film formed on the surface of metal specimens was analyzed by surface analysis technique, FTIR spectra and SEM.

**FTIR spectra:** The carbon steel specimens immersed in various test solutions for one day were taken out and dried. The film formed on the metal surface was carefully removed and thoroughly mixed with KBr, so as to make it uniform throughout. The FTIR spectra were recorded in a Perkin – Elmer– 1600 spectrophotometer.

**Scanning electron microscopy (SEM):** The carbon steel specimens immersed in various test solutions for one day were taken out, rinsed with double distilled water, dried and subjected to the surface examination. The surface morphology measurements of the carbon steel surface were carried out by scanning electron microscopy (SEM) using HITACHI S-3000H SEM.

## Results and Discussion

**Analysis of results of weight loss study:**The calculated inhibition efficiencies (IE) and corrosion rates of SA in controlling corrosion of carbon steel immersed in sea water

both in the absence and presence of $Zn^{2+}$ ion are given in table 2. The calculated value indicates the ability of SA to be a good corrosion inhibitor. The IE is found to be enhanced in the presence of $Zn^{2+}$ ion. SA alone shows some IE. But the combination of 250 ppm SA and 50 ppm $Zn^{2+}$ shows 93% IE. This suggests a synergistic effect exists between SA and $Zn^{2+}$ ion[24-26].

**Analysis of Polarization curves:** The potentiodynamic polarization curves of carbon steel immersed in sea water in the absence and presence of inhibitors are shown in figure 2. The corrosion parameters such as corrosion potential ($E_{Corr}$), Tafel slopes (anodic slope $b_a$ and cathodic slope $b_c$), linear polarization resistance and corrosion current ($I_{Corr}$) values were calculated are given in table 3. When carbon steel is immersed in sea water the corrosion potential is – 731 mV Vs saturated calomel electrode (SCE). The corrosion current is $380 \times 10^{-6}$ $A/cm^2$. When SA (250 ppm) and $Zn^{2+}$ (50 ppm) are added to the above system the corrosion potential is shifted to the cathodic side (from -731 mV to -777 mV).

**Table-2**
**Inhibition efficiencies (IE %) obtained from SA - $Zn^{2+}$ systems, when carbon steel immersed in sea water**
**Inhibitor system:** SA + $Zn^{2+}$, **Immersion period:** 3 days, corrosion rate (mm/y) given in the paranatheses

| SA ppm | Inhibition efficiency (IE %) | | | | | |
|---|---|---|---|---|---|---|
| | $Zn^{2+}$ (ppm) | | | | | |
| | **0** | | **25** | | **50** | |
| 0 | - | (0.1124) | 12 | (0.0989) | 17 | (0.0933) |
| 50 | 7 | (0.1045) | 20 | (0.0899) | 29 | (0.0798) |
| 100 | 13 | (0.0977) | 32 | (0.0764) | 52 | (0.0539) |
| 150 | 29 | (0.0798) | 58 | (0.0472) | 60 | (0.0449) |
| 200 | 45 | (0.0618) | 64 | (0.0404) | 74 | (0.0292) |
| 250 | 50 | (0.0562) | 73 | (0.0303) | 93 | (0.0078) |

**Table-3**
**Corrosion Parameters of carbon steel immersed in sea water in the absence and presence of inhibitors obtained by polarization method**

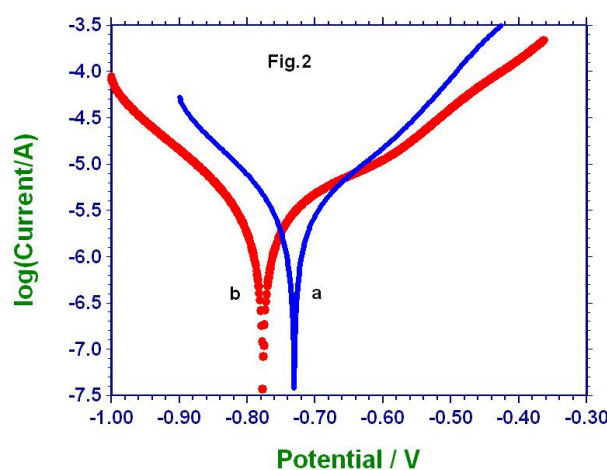| SA ppm | $Zn^{2+}$ ppm | $E_{corr}$ mV vs SCE | $b_c$ mV/decade | $b_a$ mV/decade | LPR ohm $cm^2$ | $I_{corr}$ $A/cm^2$ |
|---|---|---|---|---|---|---|
| 0 | 0 | - 731 | 135.5 | 162.3 | $1.0756 \times 10^4$ | $380 \times 10^{-6}$ |
| 250 | 50 | - 777 | 149.2 | 230.2 | $1.3848 \times 10^4$ | $362 \times 10^{-6}$ |



**Figure-2**
**Polarization curves of carbon steel immersed in various test solutions**
(a) Sea water (b) Sea water + SA (250 ppm) + $Zn^{2+}$ (50 ppm)

This suggests that the cathodic reaction is controlled predominantly. More over in presence of the inhibitor system, the corrosion current decreases from $380 \times 10^{-6}$ $A/cm^2$ to $362 \times 10^{-6}$ $A/cm^2$ and LPR value increases from $1.0756 \times 10^4$ ohm $cm^2$ to $1.2427 \times 10^4$ ohm $cm^2$. These observations indicate the formation of protective film on the metal surface [27-28].

**Analysis of FTIR spectra:** The FTIR spectrum of pure SA is shown in figure 3 (a)**.** The C=O stretching frequency of carboxyl group appears at 1707 $cm^{-1}$. The FTIR spectrum of the film formed on the metal surface after immersion in sea water consisting SA (250 ppm) and $Zn^{2+}$ (50 ppm) is shown in figure 3 (b). The C=O stretching frequency has shifted from 1707 $cm^{-1}$ to 1636 $cm^{-1}$. This indicates that the SA has coordinated with $Fe^{2+}$ on the metal surface through oxygen atom of C=O group resulting in the formation of $Fe^{2+}$ - SA complex. The peak at 1389 $cm^{-1}$ is due to Zn – O stretching. The – OH stretching frequency appears at 3429 $cm^{-1}$. These observations indicate the presence of $Zn(OH)_2$ formed on the metal surface. Thus the FTIR study leads to the conclusion that the protective film consist of $Fe^{2+}$ - OA complex and $Zn(OH)_2$ formed on the metal surface[29-32].

**Scanning Electron Microscopy (SEM):** SEM provides a pictorial representation of the surface. To understand the nature of the surface film in the absence and presence of inhibitors and the extent of corrosion of carbon steel, the SEM micrographs of the surface are examined. The SEM micrographs (X 250, X 500) of polished carbon steel surface (control) in figure 4 (a, b) shows the smooth surface of the metal. This shows the absence of any corrosion products or inhibitor complex formed on the metal surface. The SEM micrographs (X 250, X 500) of carbon steel specimen immersed in the sea water for one day in the absence and presence of inhibitor system are shown in figure 4 (c, d) and figure 4 (e, f) respectively. The SEM micrographs of carbon steel surface immersed in sea water in figure 4 (c, d) shows the roughness of the metal surface which indicates the corrosion of carbon steel in sea water. figure 4 (e, f) indicates that in the presence of 250 ppm SA and 50 ppm $Zn^{2+}$ mixture in sea water, the surface coverage increases which in turn results in the formation of insoluble complex on the surface of the metal. In the presence of SA and $Zn^{2+}$, the surface is covered by a thin layer of inhibitors which effectively control the dissolution of carbon steel[33-36].
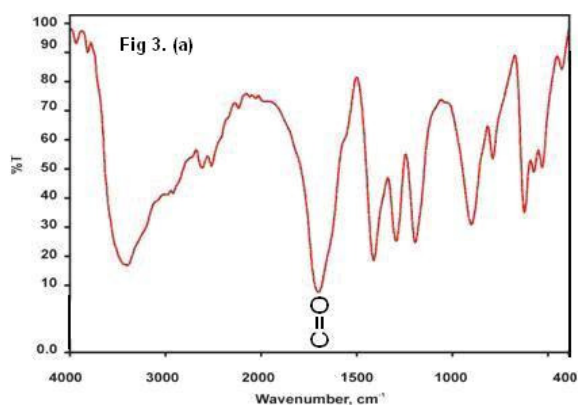


**Figure 3 (a)**
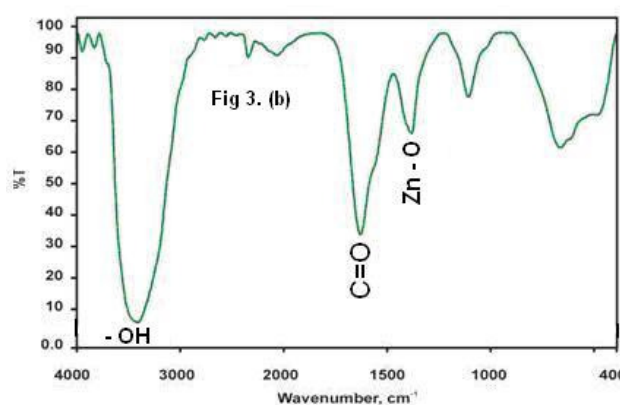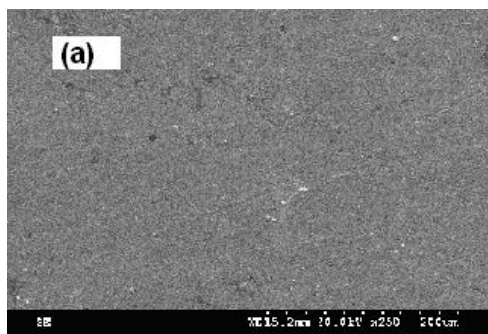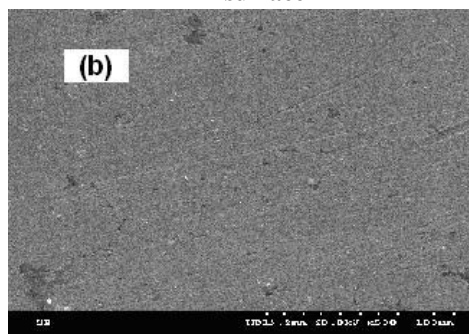**FTIR Spectrum of pure SA**



**Figure 3 (b)**
**FTIR Spectrum of the film formed on the metal surface**



**(a) Carbon steel (control); Magnification – X 250**



**(b) Carbon steel (control); Magnification – X 500**

**Figure 4**
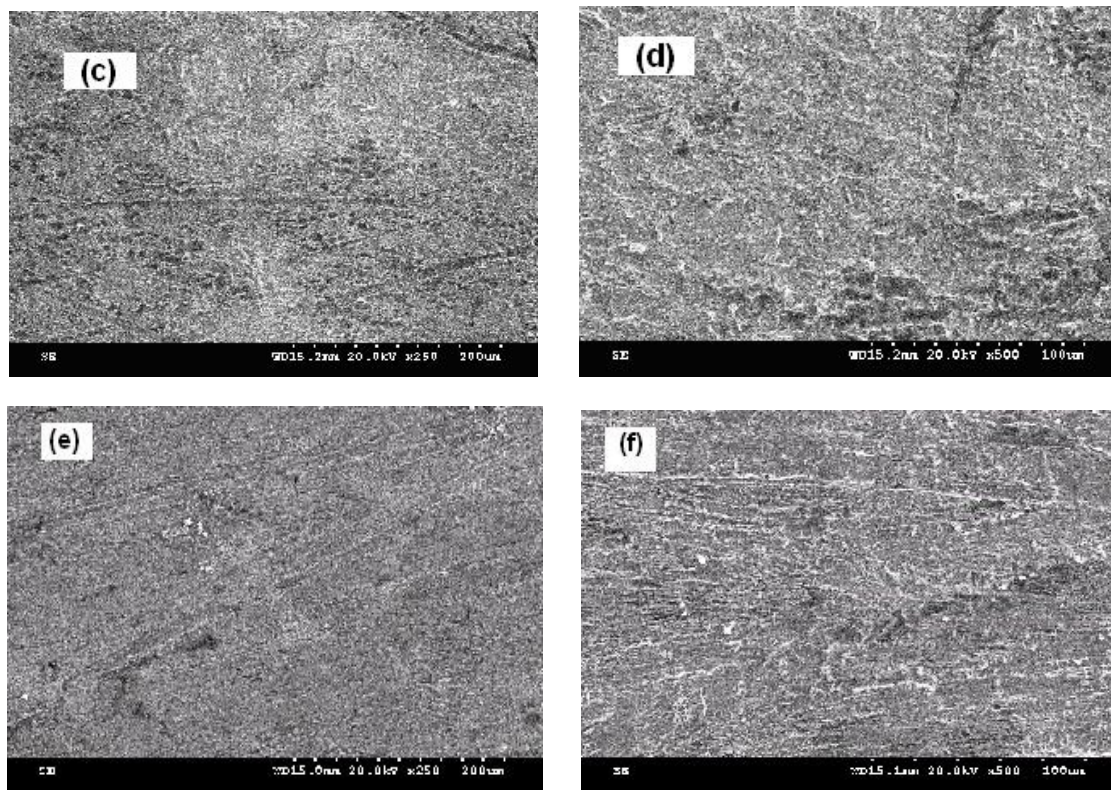**SEM micrographs of polished carbon steel (control)**

**Figure -4**
**SEM micrographs of carbon steel immersed in various test solutions**
**(a) Carbon steel immersed in sea water; Magnification – X 250**
**(b) Carbon steel immersed in sea water; Magnification – X 500**
**(c) Carbon steel immersed in sea water containing SA (250 ppm) + Zn$^{2+}$ (50 ppm); Magnification – X 250**
**(d) Carbon steel immersed in sea water containing SA (250 ppm) + Zn$^{2+}$ (50 ppm); Magnification – X 500**

**Mechanism of corrosion inhibition:** With these discussions, a mechanism is proposed for the corrosion inhibition of carbon steel immersed in sea water by 250 ppm SA and 50 ppm Zn$^{2+}$ system.

When the formulation consisting of 250 ppm of SA and 50 ppm of Zn$^{2+}$ in sea water there is a formation of SA – Zn$^{2+}$ complex in solution. When carbon steel is immersed in this solution SA – Zn$^{2+}$ complex diffuses from the bulk of the solution towards the metal surface. SA – Zn$^{2+}$ complex is converted into SA – Fe$^{2+}$ complex on the anodic sites of the metal surface with the release of Zn$^{2+}$ ion.
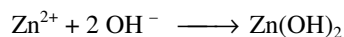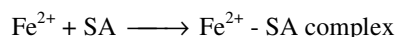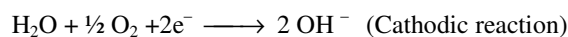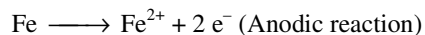
$$Zn^{2+} – SA + Fe^{2+} \longrightarrow Fe^{2+} – SA + Zn^{2+}$$
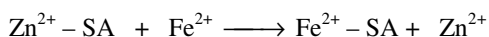
The released Zn$^{2+}$ combines with OH$^-$ to form Zn(OH)$_2$ on the cathodic sites of the metal surface.

$$Zn^{2+} + 2 OH^- \longrightarrow Zn(OH)_2 \downarrow$$
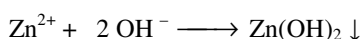
Thus the protective film consists of Fe$^{2+}$ – SA complex and Zn(OH)$_2$.

In near neutral aqueous solution the anodic reaction is the formation of Fe$^{2+}$. This anodic reaction is controlled by the formation of SA–Fe$^{2+}$ complex on the anodic site of the metal surface. The cathodic reaction is the generation of OH$^-$. It is controlled by the formation of Zn(OH)$_2$ on the cathodic sites of the metal surface.

$$Fe \longrightarrow Fe^{2+} + 2 e^- \text{ (Anodic reaction)}$$

$$H_2O + \tfrac{1}{2} O_2 + 2e^- \longrightarrow 2 OH^- \text{ (Cathodic reaction)}$$

$$Fe^{2+} + SA \longrightarrow Fe^{2+} \text{ - SA complex}$$

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

This accounts for the synergistic effect of SA – Zn$^{2+}$ system.

## Conclusions

The inhibition efficiency (IE) of SA in controlling corrosion of carbon steel immersed in sea water in the absence and presence of Zn$^{2+}$ has been evaluated by weight loss method.

The formulation consisting of 250 ppm SA and 50 ppm $Zn^{2+}$ has 93% corrosion inhibition efficiency. Polarization study reveals that SA – $Zn^{2+}$ system controls the cathodic reaction predominantly. FTIR spectra reveal that the protective film consists of $Fe^{2+}$ – SA complex and $Zn(OH)_2$. The SEM micrographs confirm the formation of protective layer on the metal surface.

## Acknowledgement

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