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## Influence of sodium potassium tartarate on 2-CIEPA -Zn<sup>2+</sup> system on the corrosion of steel in sea water

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### ABSTRACT

The inhibitive effect of 2-chloroethylphosphonic acid(2-CIEPA), zinc sulphate and sodium potassium tartarate(SPT) on the corrosion inhibition of carbon steel in seawater environment has been evaluated by classical weight loss method. The formulation consisting of 100 ppm of 2-CIEPA, 20 ppm of Zn<sup>2+</sup> and 300 ppm of SPT offer 98% inhibition efficiency. A synergistic effect exists between the 2-CIEPA- Zn<sup>2+</sup> -SPT system. The polarization study reveals that the formulations control the cathodic reaction predominantly. The AC impedance spectra confirm the protective film formed on the surface of carbon steel. FTIR spectra led to conclusion that the protective film consists of Fe<sup>2+</sup> - 2-CIEPA complex, Fe<sup>2+</sup> - SPT complex and Zn(OH)<sub>2</sub>. The 2-CIEPA- Zn<sup>2+</sup> -SPT formulation system may find applications in cooling water system.

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**Key Words :** Carbon steel, 2-chloroethylphosphonic acid, sodium gluconate, Inhibition efficiency, protective film;

## INTRODUCTION

The carbon steel is major utilized in most structural shapes such as beams, plates, bars and pipes used both onshore and offshore. Considering the severity of the structural damage caused by corrosion in various engineering field, there is the need to retard the corrosion rate, if not to prevent it completely. The corrosion inhibitor method is control the metallic surface from corrosion. The study of corrosion inhibitors such as sodium gluconate, sodium benzoate, ammonium molybdate inhibited the corrosion of steel or alloys in sea water environment[1-7]. The other organic compounds and several carboxylates such as sodium molybdate[8,9] sodium salicylate, sodium cinnamate, adipate and phosphonic acid have been used as inhibitors[10-12]. Synergistic effect of succinic acid and  $Zn^{2+}$  in controlling corrosion of carbon steel in well water has been reported [13]. Several phosphonic acids have used as corrosion inhibitor [14-18]. The present work is undertaken:

1. To evaluate the inhibition efficiency (IE) of 2-chloroethylphosphonic acid- $Zn^{2+}$  system in controlling corrosion of carbon steel immersed in sea water by weight loss method.
2. To enhance the IE, the additive SPT added to 2-CIEPA- $Zn^{2+}$  system.
3. To investigate the type of inhibitors and its protective formation on the metal surface analysed by polarization study and AC impedance study.
4. To analyse the nature of protective film by FTIR spectra.
5. To propose the mechanism of corrosion inhibition based on the above results.

## MATERIALS AND METHODS

### Preparation of the specimen

Carbon steel (0.026%S, 0.06%P, 0.4%Mn, 0.1% C, and the rest Fe) specimen of dimension 1 cm x 4 cm x 0.2 cm were used for weight loss study. Carbon steel specimens polished to mirror finish with help of emery paper of different grade and degreased with trichloroethylene.

### Weight loss method

*Int J Nano Corr Sci and Engg* **2(6) (2015) 120-130**

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Carbon steel specimens in triplicate were immersed in 100 ml of water in seawater containing various concentrations of the inhibitors, in the absence, presence of zinc sulphate, for a period of one day. The parameters of sea water is given in Table 1.

**Table 1: Parameters of seawater**

Parameter	Result
TDS	39925 ppm
Electrical conductivity	59653 micro mhos/cm
Total Hardness	6095 ppm
pH	7.84
Calcium	797 ppm
Magnesium	982 ppm
Sodium	7565 ppm
potassium	1254 ppm
Chloride	17987 ppm
Sulphate as SO <sub>4</sub>	1428 ppm

The weight of the specimens before and after immersion was determined using Shimadzu balance, AY62 model. The corrosion products were cleansed with Clarke's solution[19]. The corrosion rates (CR) of the metal specimens were calculated with the help of the following relationship:

$$\text{where } CR = \frac{\Delta m}{A * t} \quad (1)$$

CR - corrosion rate

$\Delta m$  - loss in weight (mg)

A - surface area of the specimen (dm<sup>2</sup>)

t - Period of immersion (days)

The inhibition efficiency (IE) was then calculated using the equation

$$\text{Where, } IE = 100 \left( 1 - \frac{W_2}{W_1} \right) \quad (2)$$

are the corrosion rates in the absence and presence of the inhibitor respectively.

**Int J Nano Corr Sci and Engg 2(6) (2015) 120-130**

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### **Polarization study**

Polarization studies were carried out by using CHI electrochemical impedance analyzer, model 660A. A three electrode cell assembly was employed. The working electrode used was rectangular mild steel with one face of the electrode exposed and the rest shielded with red lacquer. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode. According to the Stern-Geary equation, the steps of the linear polarization plot are substituted to get corrosion current

$$I_{\text{corr}} = b_a \times b_c / 2.303 (b_a + b_c) R_p$$

Where,  $R_p$  is polarization resistance.

The results, such as Tafel slopes ( $b_a$  and  $b_c$ ), and corrosion current ( $I_{\text{corr}}$ ) and corrosion potential ( $E_{\text{corr}}$ ) values were calculated.

### **AC impedance study**

The instrument used for polarization was also used for AC impedance study. The cell set up was the same as that used for polarization measurements. The real part and imaginary part of the cell impedance were measured in ohms at various frequencies. The values of charge transfer resistance ( $R_t$ ) and the double layer capacitance ( $C_{dl}$ ) were calculated.

### **Surface analysis**

The carbon steel specimens were immersed in various test solutions for a period of one day, the specimens were taken out, washed with distilled water and then dried. The nature of the film formed on the surface of metal specimens was analysed by the following techniques.

### **FTIR Spectra**

The film formed on the carbon steel carefully removed with sharp edged glass rod, mixed thoroughly with KBr and made into pellets, and the FTIR spectra recorded on a Perkin-Elmer 1600 spectrophotometer.

## **RESULTS AND DISCUSSION**

### **Analysis of results of mass loss method**

*Int J Nano Corr Sci and Engg* **2(6) (2015) 120-130**

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The inhibition efficiency of 2-Chloroethylphosphonic acid (2-CIEPA) –  $Zn^{2+}$  system in controlling corrosion of carbon steel in sea water (Table 2 & 3) has been evaluated by weight-loss method.

**Table 2. Corrosion inhibition efficiency of carbon steels in seawater in the presence of inhibitor obtained by mass loss method.**

S. No	$Zn^{2+}$ (ppm)	IE %
1	0	0
2	10	8
3	20	14
4	30	16
5	40	19
6	50	21

**Table 3. Corrosion inhibition efficiency of carbon steels in seawater in the presence of inhibitor obtained by mass loss method.**

S.No	$Zn^{2+}$ (ppm)	2-CIEPA (ppm)	IE %
1	0	0	0
2	20	50	51
3	20	100	62
4	20	150	73
5	20	200	79
6	20	250	88
7	20	300	92

It is observed that 2-CIEPA alone has some inhibition efficiency. Increasing the concentration of 2-CIEPA in presence of  $Zn^{2+}$  shows better inhibition efficiency. For

example, 100 ppm of 2-CIEPA and 20 ppm of  $Zn^{2+}$  62 % IE. This is due to a synergistic effect exists between 2-CIEPA and  $Zn^{2+}$  system.

#### **Influence of sodium potassium tartarate on 2-CIEPA – $Zn^{2+}$ system**

The influence of sodium potassium tartarate (SPT) on the IE of the 2-CIEPA –  $Zn^{2+}$  system in seawater environment is shown in Table 4. The addition of SPT on the best inhibitor system, increase the IE gradually. But at higher concentration, this offer very high IE. It is evident from the table 4 that when 300 ppm of SPT is added, the IE increases from 62% to 98%. The mixed inhibitors show better IE than individuals.

**Table 4. Corrosion inhibition efficiency of carbon steels in seawater in the presence of inhibitor obtained by mass loss method.**

S. No	$Zn^{2+}$ (ppm)	2-CIEPA (ppm)	SPT (ppm)	IE %
1	0	0	0	--
2	20	100	50	73
3	20	100	100	78
4	20	100	150	86
5	20	100	200	92
6	20	100	250	96
7	20	100	300	98

#### **Analysis of polarization study**

The polarization curves of carbon steel immersed in sea water in the absence and presence of inhibitors are shown in figure 1. The corrosion parameters are given in Table 5. When carbon steel is immersed in sea water the corrosion potential( $E_{corr}$ ) is -784 mV vs SCE. In the presence of the inhibitor system (100 ppm of 2-CIEPA + 20 ppm of  $Zn^{2+}$  + 300 ppm of SPT), the corrosion potential is shifted to -869 mV vs SCE. This indicates that the corrosion potential shifts to cathodic side.

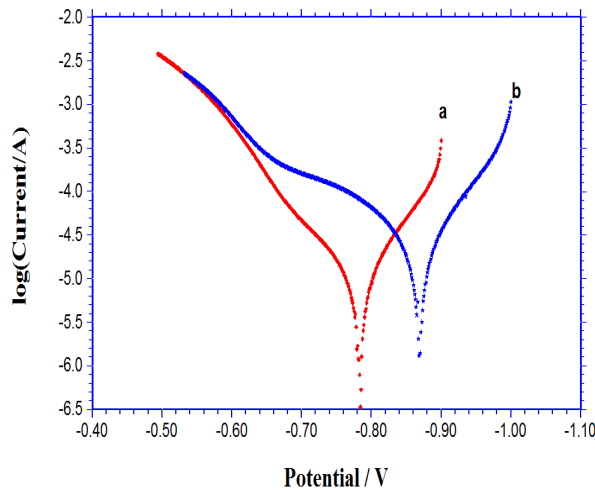
**Table 5 : Corrosion parameters of carbon steel immersed in various test solution obtained by polarization method.**

*Int J Nano Corr Sci and Engg 2(6) (2015) 120-130*

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Description	$E_{\text{corr}}$ mV/decade	$b_a$ mV/decade	$b_c$ mV/decade	$I_{\text{corr}}$ A/cm <sup>2</sup>
Sea water	-784	110	78	26.20 $\times 10^{-6}$
Sea water containing 20 ppm of Zn <sup>2+</sup> + 100 ppm of 2-CIEPA + 300 ppm of SPT	-869	197	86	1.03 x $10^{-6}$



**Figure 1: Polarization curves of carbon steel immersed in various test solution**

- Sea water
- Sea water containing 100 ppm of 2- CIEPA + 20 ppm of Zn<sup>2+</sup> + 300 ppm of SPT

This suggests that in the presence of Zn<sup>2+</sup>, the inhibitors namely, 2-CIEPA and SPT are much transported towards the metal surface and deposited on the metal surface as Fe<sup>2+</sup>-2-CIEPA complex and Fe<sup>2+</sup>-SPT complex. The anodic and cathodic Tafel slopes are different for the inhibitor systems (197mV and 86 mV). This suggests that the 2-CIEPA - Zn<sup>2+</sup> - SPT system control the cathodic reaction predominantly. The corrosion current( $I_{\text{corr}}$ ) for sea water is  $26.20 \times 10^{-6}$  A/ cm<sup>2</sup>. But for the best inhibitor system, the corrosion current value is drastically

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decreases ( $1.03 \times 10^{-6} \text{ A/cm}^2$ ). This indicates the 2-CIEPA -  $\text{Zn}^{2+}$  - SPT system forms the protective layer on the metal surface.

### Analysis of AC impedance Study

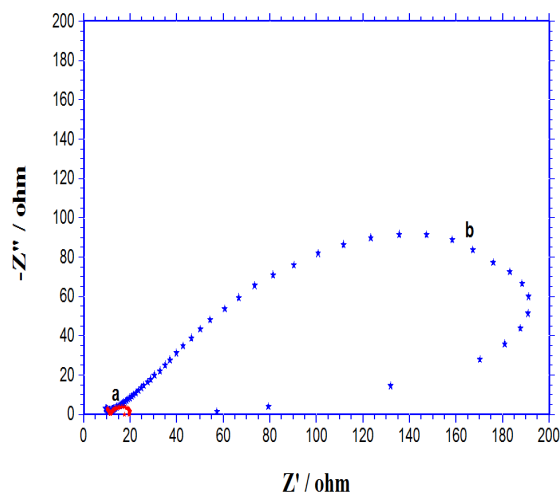
The AC impedance spectra of carbon steel immersed in various test solution are shown in Figure 2. The charge transfer resistance ( $R_t$ ) and double layer capacitance ( $C_{dl}$ ) are given in Table 6.

**Table 6 : Corrosion parameters of carbon steel immersed in various test solution obtained by AC impedance study.**

System	$R_t$ ( $\Omega \text{ cm}^2$ )	$C_{dl}$ ( $\text{F/cm}^2$ )
Sea water	8.15	$50.00 \times 10^{-6}$
Sea water containing 20 ppm of $\text{Zn}^{2+}$ + 100 ppm of 2- CIEPA + 300 ppm of SPT	202.34	$0.09 \times 10^{-6}$

When carbon steel is immersed in seawater, the  $R_t$  value is  $8.15 \Omega \text{ cm}^2$  and  $C_{dl}$  value is  $50 \times 10^{-6} \text{ F/cm}^2$ . In the presence of inhibitor system (100 ppm of 2-CIEPA + 20 ppm of  $\text{Zn}^{2+}$  + 300 ppm of SPT), the  $R_t$  value increases from  $8.15 \Omega \text{ cm}^2$  to  $202.34 \Omega \text{ cm}^2$  and the  $C_{dl}$  value decreases from  $50 \times 10^{-6} \text{ F/cm}^2$  to  $0.09 \times 10^{-6} \text{ F/cm}^2$ . This confirms the formation of a protective film on the metal surface.



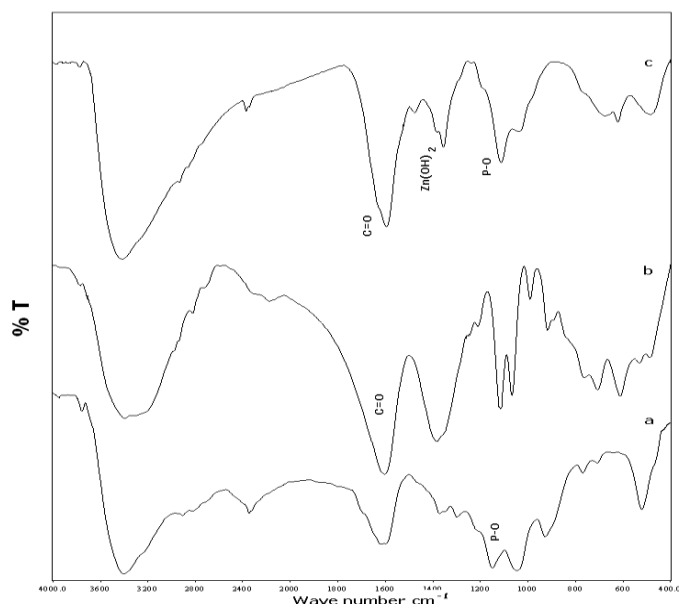


**Figure 2: AC impedance spectra of carbon steel immersed in various test solution**

- a. Sea water
- b. Sea water containing 100 ppm of 2- CIEPA + 20 ppm of  $Zn^{2+}$  + 300 ppm of SPT

### Analysis of FTIR spectra

The FTIR spectrum of pure 2-CIEPA is shown in Figure 3a. The P-O stretching frequency of phosphonic acid group appears at  $1159\text{ cm}^{-1}$ . The FTIR spectrum of pure sodium potassium tartarate is shown in figure 3b. The C=O stretching frequency of carboxyl group appears at  $1604\text{ cm}^{-1}$ . The FTIR spectrum (KBr pellet) of the film formed on the carbon steel surface after immersion in the water containing 300 ppm of SPT, 20 ppm of  $Zn^{2+}$  and 100 ppm of 2-CIEPA in the seawater environment is shown in figure 3c. The P-O stretching frequency has increased from  $1159\text{ cm}^{-1}$  to  $1110\text{ cm}^{-1}$ . This shift is caused by the electron cloud density from the oxygen atom to  $Fe^{2+}$ , it is suggested that oxygen atom of the phosphonic acid is coordinated to  $Fe^{2+}$ , resulting in the formation of  $Fe^{2+}$  - 2-CIEPA complex on the metal surface. In the case of SPT, the C=O stretching frequency has decreased from  $1604\text{ cm}^{-1}$  to  $1592\text{ cm}^{-1}$ . This indicates that carboxyl group of SPT has coordinated with  $Fe^{2+}$  on the anodic sites of the metal surface, resulting in the formation of  $Fe^{2+}$  - SPT complex. The peak at  $1362\text{ cm}^{-1}$  is due to  $Zn(OH)_2$  formed on the cathodic sites of the metal surface[20,21]. The FTIR spectra led to conclusion that the protective film consists of  $Fe^{2+}$  - SPT complex,  $Fe^{2+}$  - 2-CIEPA complex and  $Zn(OH)_2$ .



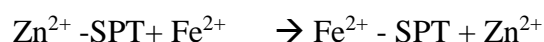
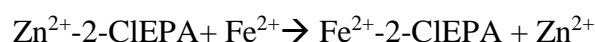
**Figure 3. FTIR spectra of:**

- (a) Pure 2-CIEPA
- (b) Pure Sodium potassium tartarate
- (c)  $\text{Zn}^{2+}$  (20 ppm), 2-CIEPA (100 ppm) and SPT (300 ppm)

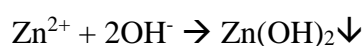
### Mechanism of corrosion inhibition

The Weight – loss study showed that the 100 ppm of 2-CIEPA, 20 ppm of  $\text{Zn}^{2+}$  and 300 ppm of SPT offer excellent inhibition efficiency. The results obtained from AC impedance, polarization study and FTIR spectra support the classical weight loss method. A corrosion inhibition mechanism proposed based on these studies[22].

- When the sea water consisting of 100 ppm of 2-CIEPA, 20 ppm of  $\text{Zn}^{2+}$  and 300 ppm of SPT are prepared, there is a formation of  $\text{Zn}^{2+}$  -2-CIEPA complex and  $\text{Zn}^{2+}$  - SPT complex in solution.
- When the carbon steel introduced in this solution, there is diffusion of zinc complexes move towards the carbon steel surface.
- On the carbon steel surface, zinc complex is converted into iron complex on the anodic site.



- The released  $\text{Zn}^{2+}$  combined with  $\text{OH}^-$  to form  $\text{Zn(OH)}_2$  on the cathodic Sites.



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- Thus, protective film consists of  $\text{Fe}^{2+}$  - 2-CIEPA complex,  $\text{Fe}^{2+}$ - SPT complex and  $\text{Zn}(\text{OH})_2$ .

## CONCLUSION

The present study leads to the following conclusions:

- ✓ A synergistic effect exists between 2-CIEPA and  $\text{Zn}^{2+}$  in controlling corrosion of carbon steel immersed in seawater.
- ✓ The formulation consisting of 300 ppm of SPT, 20 ppm of  $\text{Zn}^{2+}$  and 100 ppm 2-CIEPA provided 98% IE.
- ✓ Polarization study suggests that an inhibitors function controls the cathodic reaction predominantly.
- ✓ AC impedance spectra reveal that a protective film is formed on the metal surface.
- ✓ FTIR spectra show that the protective film consists of  $\text{Fe}^{2+}$  – 2-CIEPA complex,  $\text{Fe}^{2+}$  – SPT complex and  $\text{Zn}(\text{OH})_2$ . This formulation may find applications in cooling water system.

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*Int J Nano Corr Sci and Engg* **2(6) (2015) 120-130**

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