

Inhibition of Carbon Steel Corrosion by DTPMP – SPT – Zn²⁺ System

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Abstract- With the objective of developing a new eco-friendly inhibitor formulation for the corrosion of carbon steel on neutral aqueous solution containing 60 ppm Cl⁻. The phosphonic acid {diethylenetriamine penta(methylene phosphonic acid)}(DTPMP) was chosen as the inhibitor, which gives the inhibition efficiency of 93%. Many phosphonic acids are used as good corrosion inhibitors like ATMP, HEDP and DTPMP etc. Among which we have used the DTPMP as a potent corrosion inhibitor for this study. Because it contains number hetero atoms like Oxygen and Nitrogen. The Sodium potassium Tartrate (SPT) which is an environment friendly and used as the first synergist, Zn²⁺ may be second synergist so it may used as a ternary inhibitor system. When DTPMP used alone shows some inhibition efficiency. If we combine with the formulation of 60 ppm Cl⁻, 50 ppm DTPMP, 25 ppm SPT, and 10 ppm Zn²⁺, it gives maximum inhibition efficiency. From FTIR spectra it was observed that the protective film is formed on the metal surface. EIS spectra also confirms the formation of protective film on the metal.

Index Terms- Electrochemical studies, Inhibitors, Phosphonic acid, protective film, SEM, Synergism

I. INTRODUCTION

The inhibitors are used to protect the metals from corrosion. In general for industrial applications large number of inhibitors are used like organic compounds, amines, heterocyclic compounds and phosphonic acids etc^{1,2}. The use of polyphosphates and their derivatives has received considerable attention. These compounds are used as good inhibitors in absence of toxic nature. The very low concentrations of inhibitors (ppm) level are used to protect the large water supply system. These type of inhibitors are used in cooling water treatment^{3,4}. They are good complexing agents; they also used as corrosion inhibitors in concrete and anti-freezing coolants⁵. The phosphonic acid alone gives some inhibition efficiency. But some co-inhibitors and additives are also to be used to enhance the percentage efficiency of inhibition⁶. Further the inhibition efficiency was improved by using bivalent cations like Zn²⁺^{7,8}. The formation of protective film can be analyzed by FT-IR and EIS analysis. The suitable mechanism was proposed for the corrosion inhibition.

II. EXPERIMENTAL

2.1 Preparation of Carbon Steel Specimen

Carbon steel specimen were taken from the single sheet of Carbon Steel with the composition (C – 0.188% , S – 0.016 % , Si – 0.346 % , Mn – 1.15% , P – 0.036 % , Cr – 0.557% , Mo – 0.225 % , Ni – 0.0847% , Al – 0.0417% , Cu- 0.0342% , Ti- 0.0149% , V – 0.0313% , Pb- 0.0006% and rest Iron 97.27%) were used for weight-loss study, specimen of the size 1.0 cm x 0.2 cm x 4.0 cm were cut, polished to mirror finish by table grinding wheels, degreased with Trichloroethylene. The environment chosen for the study is 60 ppm Cl⁻.

2.2 Preparation of the solutions:

Sodium salt of Phosphonic acid (DTPMP)

0.5 g of DTPMP was dissolved in water by using triple distilled water and made up to 100 mL in a standard measuring flask. 1 mL of this solution was diluted to 100 mL to get 50 ppm of DTPMP⁹

Sodium potassium tartrate solution

0.5 g of SPT was dissolved in triple distilled water and made it up to 100 mL in a standard measuring flask. 1 mL of this solution was diluted to 100 mL to get 50 ppm of Sodium potassium tartrate.

Zinc Sulphate solution

Exactly 0.44 g of Zinc sulphate was dissolved in triple-distilled water and makes it up to 1 liter. A hundred – fold dilution yields exactly 10 ppm of Zn²⁺ ion concentration.

2.3 Weight – Loss Measurement

The Carbon Steel specimens were taken from the single sheet of Carbon Steel in Triplicate was immersed in the environment of 60 ppm Cl⁻ with and without inhibitor. The metal specimens were weighed accurately with the Denver Analytical Balance – TP 214 DE. After the immersion of metal specimen in 60 ppm Cl⁻ , the metal were taken out, rinsed in running tap water and kept in

desiccators. The corrosion products were cleaned with Clark's solution. The Corrosion rate and Inhibition Efficiency were calculated using the following relations from the difference of weight before and after the immersion.

$$I. E = X 100 \frac{W_o - W_i}{W_o} \%$$

W_o = Weight – loss in absence of an inhibitor, W_i = Weight – loss in presence of an inhibitor.

$$CR = \frac{534 \times \text{Loss in Weight (mg)}}{D (\text{g/cm}^3) \times A (\text{in}^2) \times T (\text{Hrs})} \text{ (mpy)}$$

D – Density of the metal specimen (g/cm³), A – Area of the specimen in in², T – Immersion time in Hours

2.4 Electrochemical Impedance Spectra

The electrochemical measurements presented in this study were performed using the Electrochemical Workstation (Model No. CHI760, CH Instruments, USA). Prior to the electrochemical measurements, the metal specimens were prepared according to the above described procedure. The real part (Z') and the imaginary part (Z'') of the cell impedance were measured. The Charge transfer resistance (R_{ct}) and Double layer Capacitance (C_{dl}) value were measured using the following relation.

$$C_{dl} = \frac{1}{2 \pi f R_{ct}}$$

2.5 Synergism Parameter

The inhibitors used alone which gives some inhibition efficiency. If it combines with other inhibitors, the inhibition efficiency is getting improved. This change in inhibition efficiency explained as the synergism^{10,11}. The synergism parameter can be calculated by using the equation indicated the synergistic effect existing between the inhibitors. SI value is found to be greater than one suggesting that the synergistic effect between the inhibitors.

$$S_1 = |1 - I_{1+2} / 1 - I_{1+2}|$$

I₁ – Inhibition efficiency of the inhibitor 1, I₂ – Inhibition efficiency of the inhibitor 2,
 I₁₊₂ – Combined Inhibition efficiency of inhibitor 1 and 2.

2.6 Surface Examination studies

The Carbon Steel specimens were immersed in blank as well as inhibitor solutions, for a period of three days. After the immersion period is over, the specimens were taken out and dried. The nature of the thin film formed on the surface of the metal specimens was analyzed by various surface analysis techniques.

2.6.1 FT-IR spectra

Shimadzu IR affinity – 1 KBr dei set method spectrophotometer the film formed on the Carbon steel specimen were taken out, dried and the film was carefully removed, mixed thoroughly with KBr and made in to pellets and the FT-IR spectra were recorded.

III. RESULTS AND DISCUSSION

3.1 Evaluation of synergistic effect of DTPMP with SPT-Zn²⁺ system

The environment chosen for this study was 60 ppm Cl⁻. Where, it can found that the inhibition efficiency (IE) and Corrosion Rate (CR) of DTPMP, SPT in inhibiting the corrosion of carbon steel immersed for a period of three days in the absence and the presence of Zn²⁺ is given in Table 1. It was observed from the data that SPT alone shows some IE and Zn²⁺ alone has some IE. In the absence of SPT, the rate of transport of Zn²⁺ from the bulk of the solution towards the metal surface is slower than the rate of the corrosion process on the metal surface. Hence the lower corrosion inhibition takes place in the absence of SPT, Similar observation has already been reported^{12,13}. When SPT is combined with Zn²⁺ ions, it is found that the IE increases. For example, 25 ppm SPT has only 8 % IE and 10 ppm Zn²⁺ has only 24 % interestingly, their combination shows 45 % IE. This suggests a synergistic effect between the binary inhibitor formulation SPT and Zn²⁺ ions; SPT is able to transport Zn²⁺ towards the metal surface. The role of DTPMP in the ternary inhibitor formulation, experiments was conducted with DTPMP alone, SPT and with Zn²⁺, DTPMP with various concentrations. The highest inhibition efficiency with these systems is shown in the Table 1. 50 ppm DTPMP, 25 ppm SPT and 10 ppm Zn²⁺ gives maximum inhibition efficiency, which will not obtained even at higher concentrations. This confirms the synergistic effect is offered between the inhibitors. Thus, it may be concluded that Zn²⁺ is the primary synergist and DTPMP is the secondary synergist and both play a significant synergistic role in inhibiting corrosion¹⁴. The Maximum inhibition efficiency is offered at which the lower concentrations, Hence, it was confirmed the synergistic behavior between the inhibitors. Concentration plays an important role in this system, as the concentration increases the inhibition efficiency also increases up to which a certain concentration. After that the inhibition efficiency decreases because of the dissolution of inhibitors in water itself. This maximum Inhibition Efficiency is found to identify the synergism.

TABLE. 1. Inhibition Efficiencies (IE) and Corrosion Rate (CR) of carbon steel in 60 ppm Cl⁻, the absence and the presence of inhibitors by weight – loss method

| SPT Ppm | Zn ²⁺ ppm | DTPMP ppm | Corrosion rate (mpy) | IE % |
|---------|----------------------|-----------|----------------------|------|
| 25 | 0 | 0 | 1.62 | 8 |
| 0 | 10 | 0 | 1.34 | 24 |
| 0 | 0 | 50 | 1.36 | 22 |
| 25 | 10 | 0 | 0.96 | 45 |
| 0 | 10 | 50 | 1.03 | 41 |
| 25 | 10 | 10 | 0.44 | 74 |
| 25 | 10 | 25 | 0.30 | 83 |
| 25 | 10 | 50 | 0.11 | 93 |
| 25 | 10 | 75 | 0.33 | 81 |
| 25 | 10 | 100 | 0.37 | 79 |

3.2 Synergism Parameter

Each and every inhibitor having its individual inhibition efficiency that may be high or low depends on the group of atoms present in the inhibitor molecule. If more than 1 inhibitors are used for the study, which must be checked whether the synergistic behaviour is offered between the inhibitors or not. In general, if two or more inhibitors are combined that may improve the inhibition efficiency of the system. The values of synergism parameters are shown in Table 2. The values of SI are greater than one, suggesting a synergistic effect.

S₁ approaches 1 when no interaction exists between the inhibitor compounds. When SI > 1, this leads to the synergistic effect. In the case of SI < 1, the negative interaction of inhibitors prevails. i.e. Increase in corrosion rate taking place¹⁵. Table 2.

TABLE 2. Synergism parameter of Carbon steel immersed in 60 ppm Cl⁻ in the presence and absence of inhibitor

| SPT + Zn ²⁺ (I ₂) IE % | DTPMP (I ₁) IE % | SPT-Zn ²⁺ - DTPMP (I' ₁₊₂) IE % | S _I |
|---|------------------------------|--|----------------|
| 45 | 15 | 74 | 8.43 |
| 45 | 25 | 83 | 12.87 |
| 45 | 10 | 93 | 4.30 |
| 45 | 22 | 81 | 11.55 |
| 45 | 27 | 79 | 14.66 |

3.3 Analysis of FT-IR Spectra

The FT-IR spectrum of pure DTPMP is shown in Fig. 1 b. The P – O stretching frequency appears at 1059 cm⁻¹. The C – N Stretching frequency appears at 1116 cm⁻¹ ¹⁶. P- OH group causes absorption at 3332 cm⁻¹ and P(O) OH group at 3402 cm⁻¹. The absorption band at 1059 cm⁻¹ represents P – O stretching frequency. The absorption band at 1346 cm⁻¹ represent P = O stretching. The absorption band due to the bending of O-P-O appears at 493,545, and 633 cm⁻¹. The bending vibrations (-CH₂ Scissoring) of aliphatic tertiary amine grout CH₂-N appears at 1448 cm⁻¹. The weak C-C stretching vibrations appears at 956 748,725 cm⁻¹. Thus DTPMP with molecular formula C₉H₂₈N₃O₁₅P₅ is characterized by FT-IR spectrum. The FT-IR spectrum of Pure Sodium Potassium Tartrate (SPT) is shown in Fig. 1a. The C=O stretching frequency of carbonyl group appears at 1604 cm⁻¹. The FT-IR spectrum of the film (KBr) formed on the surface of carbon steel after immersion in the test solution containing 50 ppm DTPMP, 25 ppm SPT and 10 ppm of Zn²⁺ is shown in the Fig. 1. (c). The C – N stretching frequency shifted from 1116 cm⁻¹ to 1059 cm⁻¹ and P – O stretching frequency shifted from 1059 cm⁻¹ to 1056 cm⁻¹, which suggests that oxygen and nitrogen atom of DTPMP is coordinated with Fe²⁺ on the anodic sites of the metal surface, resulting the formation of Fe²⁺ - DTPMP complex ¹⁷⁻¹⁹. The C = O stretching frequency has shifted from 1604 cm⁻¹ to 1614 cm⁻¹. This indicates that SPT has coordinated to the Fe²⁺ on the anodic sites of the metal surface. The peak at 1348 cm⁻¹ is due to Zn (OH)₂ formed on the cathodic sites. Thus FT-IR spectra lead to the conclusion that the protective film consists of Fe²⁺ - SPT and Zn (OH)₂ ^{20,21}.

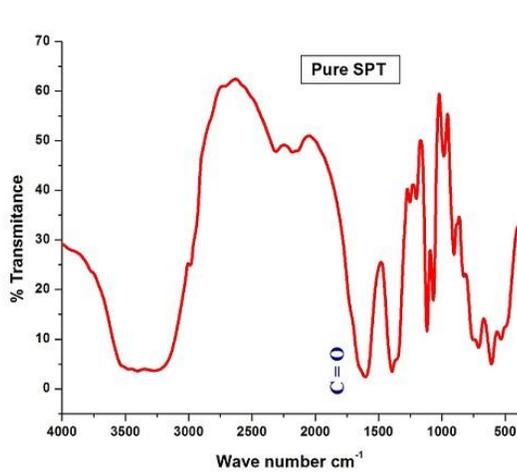


Fig.1 a Pure SPT

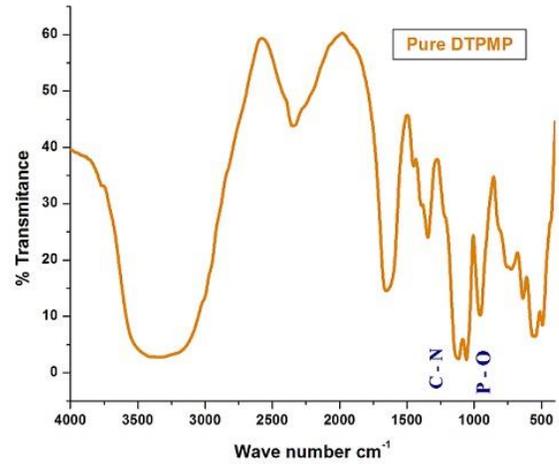


Fig 1. b Pure DTPMP

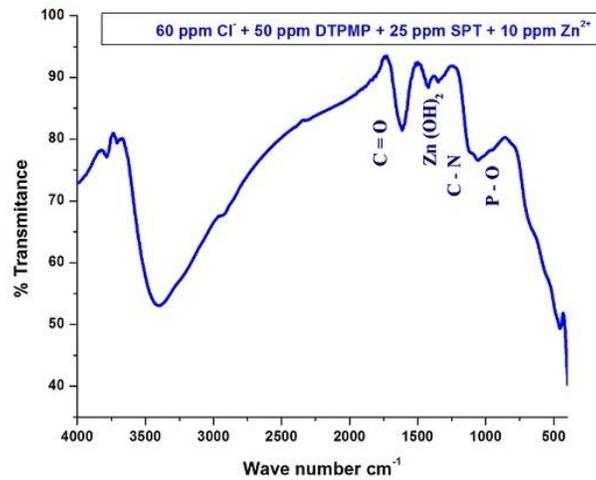


Fig 1. c 60 pp Cl⁻ + 50 ppm DTPMP + 25 ppm SPT + 10 ppm Zn²⁺

3.4 Analysis of Electrochemical Impedance Spectra (EIS)

Table 3. The EIS parameters of carbon steel immersed in various test solutions are given in Table 3.

| S.No | Cl ⁻ ppm | DTPMP ppm | SPT Ppm | Zn ²⁺ ppm | R _t Ω cm ² | C _{dl} μF / cm ² | IE % |
|------|------------------------|--------------|------------|-------------------------|-------------------------------------|---|---------|
| 1 | 60 | 0 | 0 | 0 | 215 | 6.22 x 10 ⁻⁶ | ---- |
| 2 | 60 | 50 | 25 | 10 | 2711 | 3.94 x 10 ⁻⁸ | 92 |

Fig. 2. Shows the Electrochemical Impedance Spectra

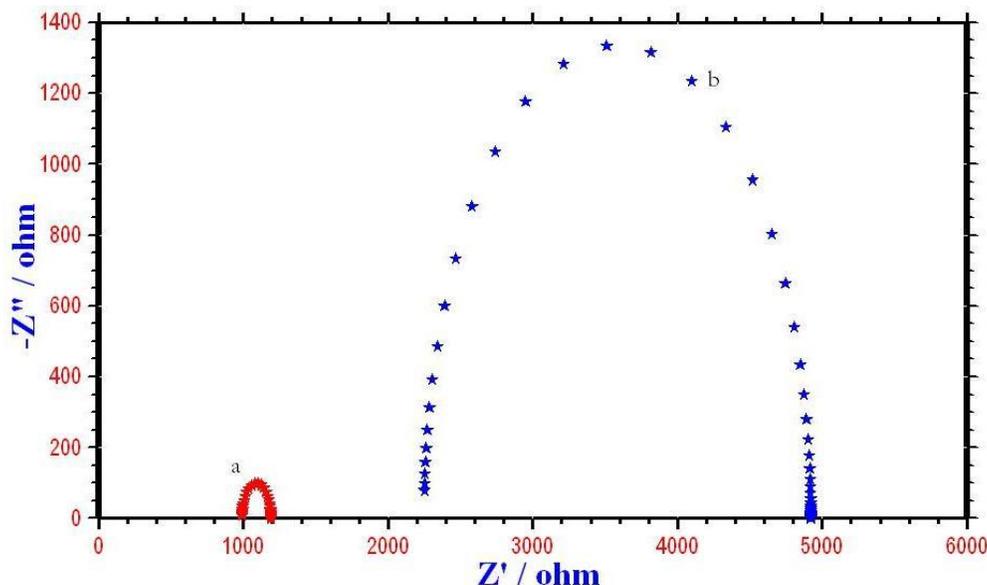


Fig.2 EIS curves of carbon steel immersed in various test solutions.

- a) 60 ppm Cl⁻
- b) 60 ppm Cl⁻ + 50 ppm DTPMP + 25 ppm SPT + 10 ppm Zn²⁺

The Nyquist representations of the impedance behaviour of carbon steel in 60 ppm Cl⁻ with and without inhibitors are given in Table 3. The existence of single semi circle showed the single charge transfer process during dissolution, which is unaffected by the presence of inhibitor. Here, for uninhibited solution the charge transfer resistance is 215 ohm cm², for inhibited solution containing 50 ppm DTPMP, 25 ppm SPT and 10 ppm Zn²⁺ the charge transfer resistance 2711 ohm cm². At the same time the double layer capacitance (C_{dl}) value getting decreases from 6.22 x 10⁻⁶ μF / cm² to 3.94 x 10⁻⁸ μF / cm². It is clear that the addition of inhibitor increases the value of charge transfer resistance (R_{ct}) and decreases the value of C_{dl}. The decreases in C_{dl} attributed to increases in thickness of electronic double layer^{22,23}. In addition to that the formation of protective film was confirmed by increase in R_{ct} value²⁴⁻²⁶. The percentage of efficiency of the inhibitor can be calculated by using following relation.

$$I.E = \frac{R'_{ct} - R_{ct}}{R'_{ct}}$$

R'_{ct} – Charge transfer resistance for inhibited solution
R_{ct} - Charge transfer resistance for uninhibited solution

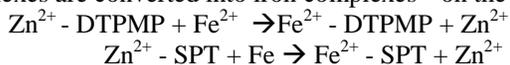
By using the above relation the percentage efficiency of the inhibitor was calculated. This inhibitor formulation gives 92 % inhibition efficiency. Thus the EIS spectral data reveal that a protective film is formed on the metal surface^{27,28}

3.5 Mechanism of Corrosion Inhibition

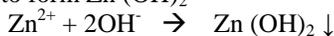
In order to explain the experimental results, the following mechanism was proposed for corrosion inhibition. The formulation consisting of 50 ppm of DTPMP, 25 ppm of SPT and 10 ppm of Zn²⁺ has 93 % Inhibition Efficiency. Polarization study reveals that the formulation functions as anodic inhibitor. Electrochemical Impedance spectra reveal that the protective film is formed on the metal surface. FT-IR spectra show that the protective film consists of Fe²⁺ - DTPMP complex.

When formulation consisting of 60 ppm Cl⁻, 50 ppm DTPMP, 25 ppm SPT and 10 ppm Zn²⁺ is prepared, there will be the formation of DTPMP-Zn²⁺ and SPT- Fe²⁺ complexes in the solution .When Carbon steel is immersed the complexes formed on the solution may diffuse to the metal.

On the Carbon steel the Zn²⁺ complexes are converted into iron complexes²⁹ on the anodic sites.



The released Zn²⁺ ions reacts with OH⁻ ions to form Zn (OH)₂



Thus the protective film consists of Fe²⁺ - DTPMP, Fe²⁺ - SPT and Zn (OH)₂ complexes. Thus Zn(OH)₂ precipitate may take place at cathodic sites thus decreasing the rate of further oxygen reduction.

IV. CONCLUSION

A formulation consisting of DTPMP, SPT and Zn^{2+} can be used as a potent inhibitor to prevent the corrosion of Carbon steel in 60 ppm Cl^- medium. DTPMP plays an excellent synergistic role in the SPT- Zn^{2+} - DTPMP system. The ternary system SPT (25ppm) – Zn^{2+} (10 ppm) – DTPMP (50ppm) is effective and it gives 93 % of Inhibition Efficiency. Significant synergism was obtained by the combined application of SPT- Zn^{2+} - DTPMP. The concentration of Zn^{2+} can be reduced by the addition of SPT. The DTPMP is an eco-friendly and is required very low concentrations. Thus this new inhibitor formulation is environment friendly. The inhibitor formulation acts as anodic inhibitor. In presence of the inhibitor, the charge transfer resistance is significantly increased. Also, the double layer capacitance of surface film reduced markedly. Both SPT and DTPMP form stable complexes with metal ions in the metal surface. The protective film consists of Fe^{2+} - SPT, Fe^{2+} - DTPMP and $Zn(OH)_2$.

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