Corrosion Behaviour of Carbon Steel in DTPMP-ST-Zn^{2+} System: An Eco-Friendly System

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Abstract

Diethylenetriamine penta (methylene phosphonic acid) (DTPMP) in the presence of Zn^{2+} ions are used to functions as the corrosion inhibitors in controlling the corrosion of carbon steel in 60 ppm Cl$^-$. To reduce the toxic nature of Zn^{2+} has to add other agents like Sodium Tungstate (ST). DTPMP is environment- friendly, non-toxic and non-polluting agent is used to control the rate of corrosion. Here, the corrosion control of carbon steel in 60 ppm Cl$^-$ was investigated by Weight-loss study, electrochemical measurements and surface examination studies. The corrosion Inhibition Efficiency (IE) offered by 25 ppm of DTPMP, 25 ppm of ST, 10 ppm of Zn^{2+} was 92 %. The synergistic behaviour of inhibiting action was also calculated. Electrochemical Impedance spectra indicates that surface film formed on the carbon steel shows that high charge transfer resistance and low Double layer capacitance, which suggests the film, is non-porous and protective. Potentiodynamic polarization study shows that the system works as an cathodic inhibitor. The FT-IR spectra reveals that the protective film consists of Fe^{2+} - DTPMP complex, Fe^{2+} - ST complex and Zn(OH)$_2$ formation.

Keywords: Carbon steel, phosphonic acid, corrosion inhibition, F-Test, FT-IR spectra.

Introduction

Large number of chemicals can inhibit the corrosion of metals in neutral aqueous solutions. The metal and inhibitor having different properties for different environment. The molybdate[1,2], chromates have been used as corrosion inhibitors. Tungstate having more efficiency when compared to chromates, molybdate. Tungstate is good corrosion inhibitor for Al [3–5] and with Zinc[6] in neutral and acidic solutions. Even though it acts as a effective corrosion inhibitor, in presence of other substance like phosphonic acids[8], the inhibition efficiency will be improved. DTPMP combined with different metal ions such as Zn^{2+} *etc.*, has been used in the cooling water systems[9-14]. Corrosion inhibition and scale prohibiting properties of some phosphonic acids and DTPMP have also been investigated[15]. The inhibiting property of Diethylenetriamine penta (methylene phosphonic acid) as corrosion inhibitor in association with a cation like Zn^{2+} has been discussed[16]. The present study evaluated the synergistic effect of the sodium tungstate-Zn^{2+} system and influence of DTPMP.

Inhibition efficiency (IE) of the ST-Zn^{2+} system. The type of inhibitor is evaluated by electrochemical studies and the formation of protective film is confirmed by the FT-IR data.

Material and Methods

Preparation of Carbon Steel specimen: Carbon steel samples 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 and electrochemical measurements, 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$^-$. The Physico-chemical parameters of water used to prepare the solutions for making medium and inhibitor are given in table 1.

Table-1
Physico-chemical parameters of water used to prepare solutions

S. No.	Parameters	Level of Content
1	Appearance	Clean and Clear
2	Odour	None
3	TDS	5 ppm
4	pH	7.04
5	Total Hardness as CaCO$_3$	3 ppm
6	Chloride as Cl	2 ppm
7	Fluoride as F	Nil
8	Sulphate as SO$_4$	Nil
9	Phosphate as PO$_4$	Nil

Weight – Loss Measurement: Carbon Steel specimen in Triplicate were immersed in 60 ppm Cl$^-$ with and without inhibitor. After the immersion period is over specimens were taken out, rinsed in running tap water and kept in a desiccators. The corrosion products were cleaned with Clark's solution[17]. Then Weight – loss determined in order to calculate the

Inhibition Efficiency and Corrosion Rate (CR) using the following formulae.

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

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

$$CR = \frac{\text{Loss in Weight (mg)}}{\text{SA (dm}^2\text{) x IP (days)}}$$

SA – Surface Area of the specimen in dm^2, IP – Immersion Period in days

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 experiment was carried out at room temperature with 60 ppm Cl⁻ as an electrolyte. The platinum electrode and saturated calomel electrode (SCE) were used as auxiliary and reference electrodes respectively. Working electrode constitute Carbon steel specimen of 1 cm² area. In order to minimize the ohmic potential drop the tip of the reference electrode is positioned very close proximity to the working electrode.

Potentiodynamic polarization study was carried out at a scan rate of 0.1 mV/s. The open circuit potential (OCP) was established first and then the polarization measurement was the polarization for carbon steel specimens in the test solution with and without inhibitors. 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 calculated using the following relation.

$$C_{dl} = \frac{1}{2 \Pi R_{ct} f_{max}}$$

Surface Examination studies: The carbon steel specimens were immersed in blank as well as inhibitor solutions, for a period of 3 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.

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.

Synergism Parameter: The synergism parameter can be calculated by using the equation indicated the synergistic effect existing between the inhibitors[18]. SI value is found to be greater than one suggesting that the synergistic effect between the inhibitors.

$$SI = 1 - I_{1+2} / 1 - I'_{1+2}$$

I_1 – Inhibition efficiency of the inhibitor 1, I_2 – Inhibition efficiency of the inhibitor 2, I '$_{1+2}$ – Combined Inhibition efficiency of inhibitor 1 and 2.

Analysis of Variance (ANOVA): An F- test was carried out to investigate whether the synergistic effect existing between the inhibitor systems is statistically significant[19] is greater than 5.32 for 1, 8 degrees of freedom, the synergistic effect proves to be statistically significant. If it is less than 5.32 for 1,8 degrees of freedom, it was statistically insignificant at a 0.05 level of significance.

Results and Discussion

Weight – loss method: Evaluation of improvement of IE of Sodium Tungstate with Zn^{2+}: The inhibition efficiency (IE) of Sodium Tungstate (ST) in controlling corrosion of carbon steel immersed in 60 ppm Cl⁻ for a period of three days in the absence and the presence of Zn^{2+} is also given in Table-2. It can be seen from the data that ST alone shows some IE, Whereas Zn^{2+} alone has some IE. In the absence of ST, the rate of transport of Zn^{2+} 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 ST, Similar observation has already been reported[20]. When ST is combined with Zn^{2+} ions, it is found that the IE increases. For example, 25 ppm ST has only 11 % IE and 10 ppm Zn^{2+} has only 24 % interestingly, their combination shows 31 % IE. This suggests a synergistic effect between the binary inhibitor formulation ST and Zn^{2+} ions; ST is able to transport Zn^{2+} towards the metal surface.

Evaluation of synergistic effect of DTPMP with ST-Zn^{2+} system: In order to examine the role of DTPMP in the ternary inhibitor formulation, experiments were conducted with DTPMP alone, ST and with Zn^{2+}, DTPMP in a wide concentration range. The highest inhibition efficiency with these systems is shown in the table-2. The synergistic effect in the ST-Zn^{2+}- DTPMP system is evident from the data in table 2. The Zn^{2+} ions acts as one synergist and DTPMP acts as the other. From the date in table 2, it is seen that at relatively higher concentrations of both ST and Zn^{2+}, 92 % IE was obtained. However, such efficiency is not obtained with concentrations of ST and DTPMP, even at relatively high concentrations. Thus, it may be concluded that Zn^{2+} is the primary synergist and DTPMP is the secondary synergist and both play a significant synergistic role in inhibiting corrosion. Hence, the highest IE is obtained at such low concentrations of each of the components in the ternary inhibition formulation.

Table-2
Inhibition Efficiencies (IE) of carbon steel in 60 ppm Cl⁻, the absence and the presence of inhibitors and Inhibition efficiency (IE) obtained by weight – loss method

ST ppm	Zn^{2+} ppm	DTPMP ppm	IE %
25	0	0	11
0	10	0	24
0	0	25	10
25	10	0	31
0	10	25	36
25	10	5	45
25	10	10	58
25	**10**	**25**	**92**
25	10	50	82
25	10	75	76

Influence of immersion period on the ST-Zn^{2+} - DTPMP system: The influence of immersion period on the IE of ST (25ppm) – Zn^{2+} (10ppm)-DTPMP (25ppm) is shown in table 3. It is found that as the immersion period increases, the inhibition efficiency decreases[21]. This is due to the fact that as the immersion period increases the protective film is ruptured by the continuous attack of Cl⁻ present in the solution. There is a competition between the two processes, namely the formation of Fe-ST and Fe-DTPMP complex and iron chloride. It appears that the formation of iron chloride is more favored than the formation of iron complexes. Moreover, the iron complexes of ST and DTPMP film formed on the metal surface is converted

into iron chloride, which goes into the solution, and hence, the IE decreases as the immersion period increases.

Synergism Parameter: The values of synergism parameters are shown in table 4. The values of SI are greater than one, suggesting a synergistic effect. SI approaches 1 when no interaction exists between the inhibitor compounds. When SI > 1, this points to the synergistic effect. In the case of SI < 1, the negative interaction of inhibitors prevails i.e. Increase in corrosion rate taking place[22]. From table 4 the most values are greater than unity, suggesting that the synergistic behaviour is existing between the inhibitors.

Surface Analysis: The protective film formed on the surface of the metal in the presence of Zn^{2+}-WO_4^{2-} has been analyzed by FTIR spectroscopy.

Analysis of FTIR Spectra: The FT-IR spectrum of Pure Sodium Tungstate (ST) is shown in figure 2a. The WO_4^{2-} stretching frequency of the sodium tungstate appears at 1687 cm⁻¹. The FT-IR spectrum of Pure DTPMP is shown in figure 2b. The C – N stretching frequency appears at 1116 cm⁻¹ and P – O stretching frequency appears at 1059 cm⁻¹. The FT-IR spectrum of pure DTPMP is shown in figure 2(b). The P – O stretching frequency appears at 1059 cm⁻¹. The C – N stretching frequency appears at 1116 cm⁻¹. 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.

Table-3
Influence of Immersion Period on the IE of ST– Zn^{2+}– DTPMP system

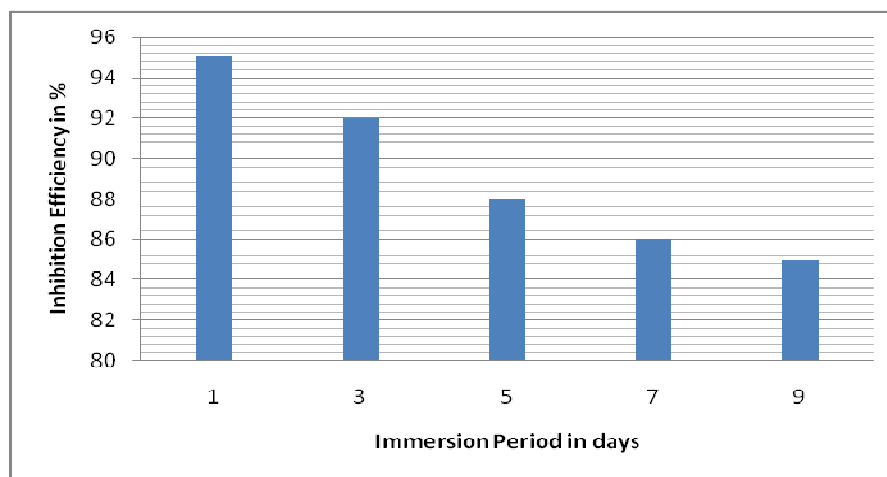| System	Immersion Period (Days)				
	1	**3**	**5**	**7**	**9**
60 ppm Cl⁻ CR (mdd)	0.0051	0.0075	0.0155	0.0295	0.0376
60 ppm Cl⁻ + ST (25ppm) + Zn^{2+}(10 ppm) + DTPMP (25 ppm)CR (mdd)	0.0003	0.0006	0.0018	0.0040	0.0054
IE %	**95**	**92**	**88**	**86**	**85**

Figure-1
**Influence of immersion period variation**

Table-4
Synergism parameter of Carbon steel immersed in 60 ppm Cl^- in the presence and absence of inhibitor

ST +Zn^{2+} (I_2) IE %	DTPMP (I_1) IE %	ST-Zn^{2+} - DTPMP (I'_{1+2}) IE %	SI
31	15	45	9.54
31	25	58	12.63
31	**10**	**92**	**2.96**
31	22	82	7.77
31	27	76	10.40

The absorption band due to the bending of O-P-O appears at 493,545, and 633 cm^{-1}. The bending vibrations (-CH$_2$ Scissoring) of aliphatic tertiary amine grout CH$_2$-N appears at 1448 cm^{-1}. The weak C-C stretching vibrations appears at 956 748,725 cm^{-1}. Thus DTPMP with molecular formula C$_9$H$_{28}$N$_3$O$_{15}$P$_5$ is characterized by FT-IR spectrum.

The FT-IR spectrum (KBr Pellet) of the film formed on the carbon steel surface after immersion in the solution containing 60 ppm Cl$^-$, 25 ppm DTPMP, 25 ppm ST and 10 ppm Zn^{2+} is shown in figure 2c. The tungstate stretching frequency of ST shifted from 1687 cm^{-1} to 1600 cm^{-1}. This suggests that WO$_4^{2-}$ of ST is coordinated with Fe^{2+} on the anodic sites of the metal surface also resulting in the formation of Fe^{2+}- WO$_4^{2-}$ complex. The C – N stretching frequency shifted from 1116 cm^{-1} to 1049 cm^{-1} and P – O stretching frequency shifted from 1059 cm^{-1} to 904 cm^{-1}, which suggests that oxygen and nitrogen atom of DTPMP is coordinated with Fe^{2+} on the anodic sites of the metal surface, resulting the formation of Fe^{2+} - DTPMP complex [23-25]. The band at 1317 cm^{-1} may be due to the in plane vibration of the OH group in Zn(OH)$_2$ formed on the cathodic sites of the metal surface[26,27].

Analysis of Electrochemical Impedance Spectra (EIS): The EIS parameters of carbon steel immersed in various test solutions are given in table 5.
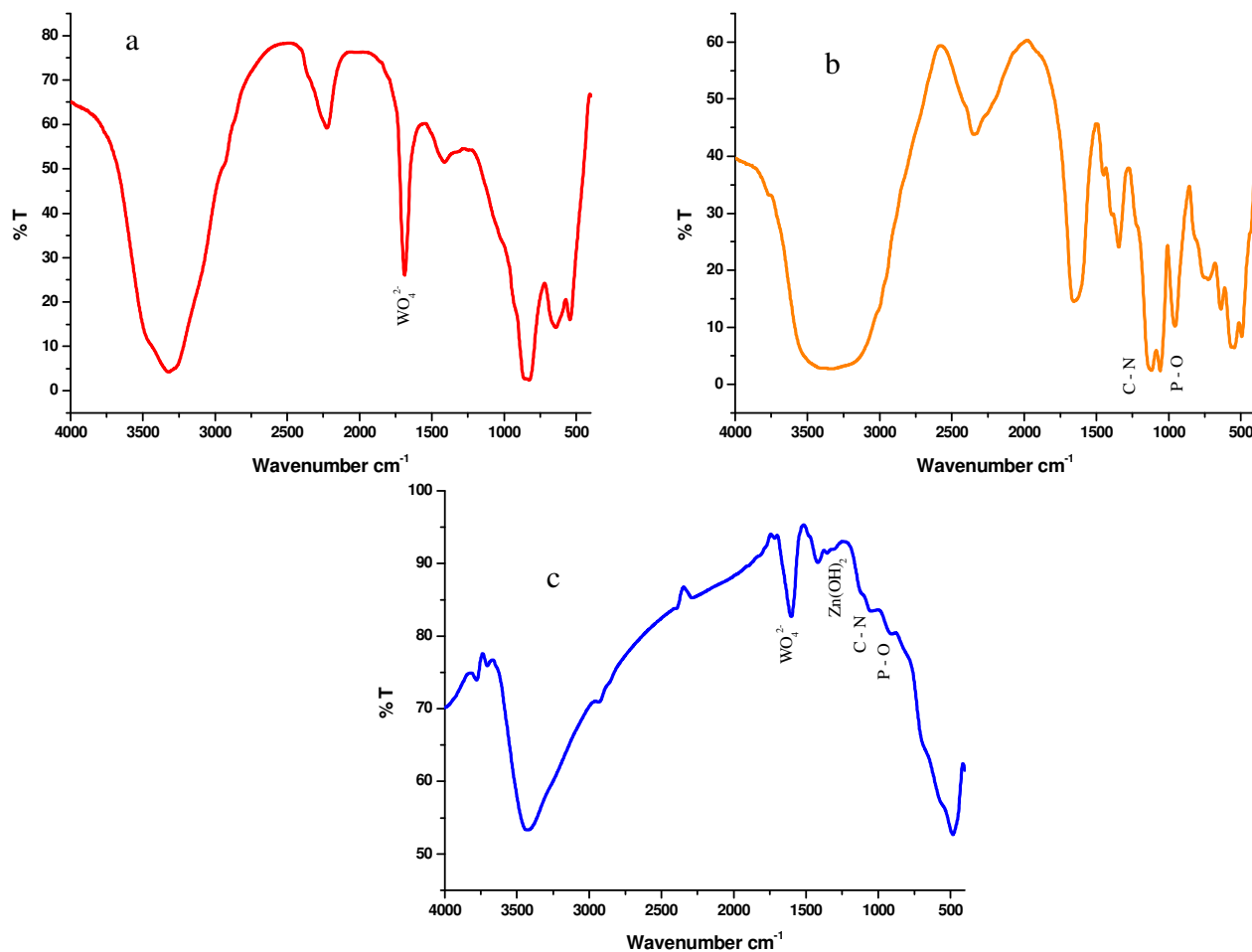
a) Pure ST b) Pure DTPMP c) Film formed on the metal surface after immersion of 60 ppm Cl$^-$ + 25 ppm DTPMP + 25 ppm ST + 10 ppm Zn^{2+}
Figure-2
FT-IR spectrum

Table-5
EIS parameters of Carbon steel immersed in 60 ppm Cl⁻ environment

S.No	Cl⁻ ppm	DTPMP ppm	ST ppm	Zn²⁺ ppm	R_t Ω cm²	C_{dl} µF / cm²	IE %
1	60	0	0	0	215	6.22×10^{-6}	---
2	60	25	25	10	3671	2.25×10^{-8}	94.14

Inhibitor System: DTPMP – ST – Zn²⁺   Immersion Period: 3 Days   pH **= 7**
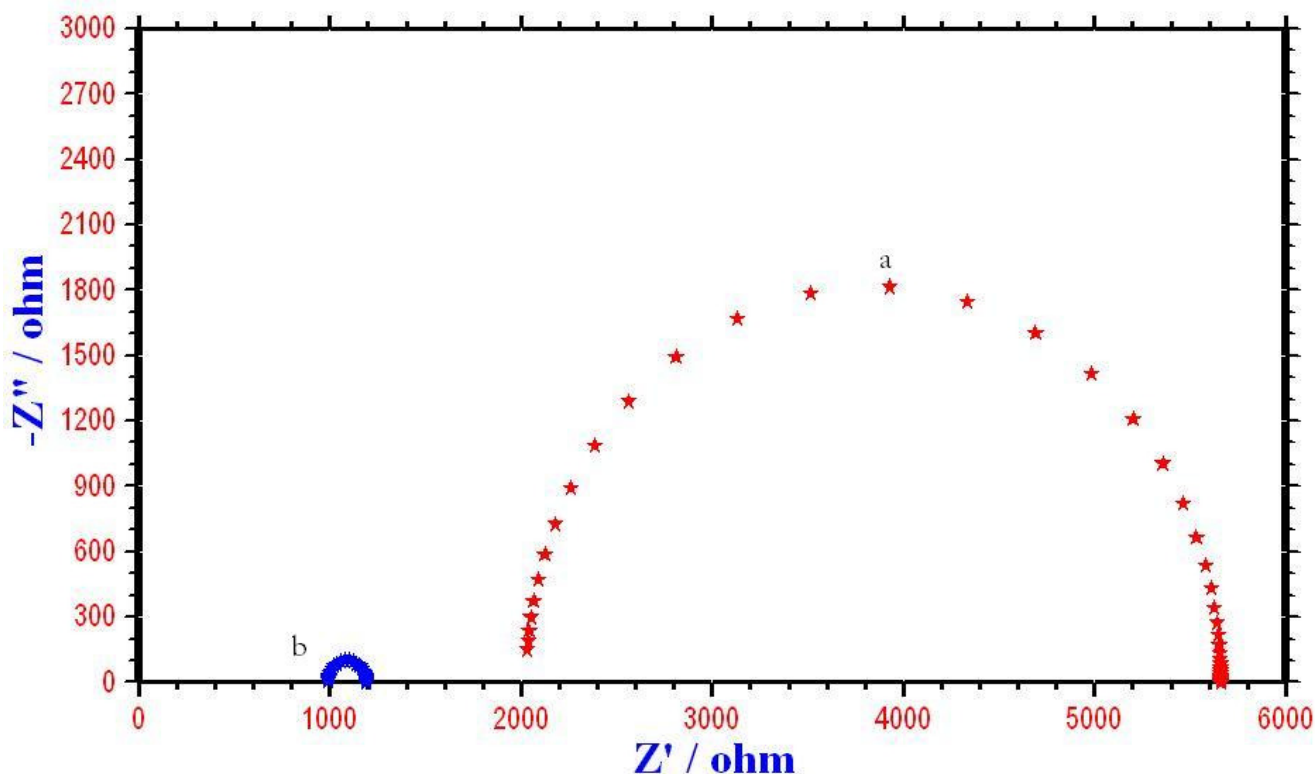

Figure-3
EIS curves of carbon steel immersed in various test solutions,
a) 60 ppm Cl⁻ b) 60 ppm Cl⁻ + 25 ppm DTPMP + 25 ppm ST + 10 ppm Zn²⁺

The Nyquist representations of the impedance behaviour of carbon steel in 60 ppm Cl⁻ with and without inhibitors are given in table 5. 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 25 ppm DTPMP, 25 ppm ST and 10 ppm Zn²⁺ the charge transfer resistance 3671 ohm cm². At the same time the double layer capacitance (C_{dl}) value getting decreases from 6.22×10^{-6} µF / cm² to 2.25×10^{-8} µF / cm² [28] . 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[29]. In addition, the formation of protective film is confirmed by increase in R_{ct} values[30,31]. The percentage of

efficiency of the inhibitor can be calculated by using following relation.

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

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 94.14 % inhibition efficiency. Thus the EIS spectral data reveal that a protective film is formed on the metal surface.

Potentiodynamic Polarization study: The corrosion parameters of carbon steel in various test solutions are given table 6.

Table-6
Corrosion parameters of carbon steel immersed in 60 ppm Cl⁻ environment obtained by the polarization study

S.No	Cl⁻ ppm	DTPMP ppm	ST ppm	Zn²⁺ ppm	E_corr. mV vs SCE	b_c mV	b_a mV	I_corr A/cm²	I E %
1	60	0	0	0	-598	5.27	5.18	1.26×10^{-5}	-
2	60	25	25	10	-442	6.18	5.33	2.79×10^{-6}	78

Inhibitor System: DTPMP – ST – Zn²⁺   Immersion Period: 3 Days   pH **= 7**
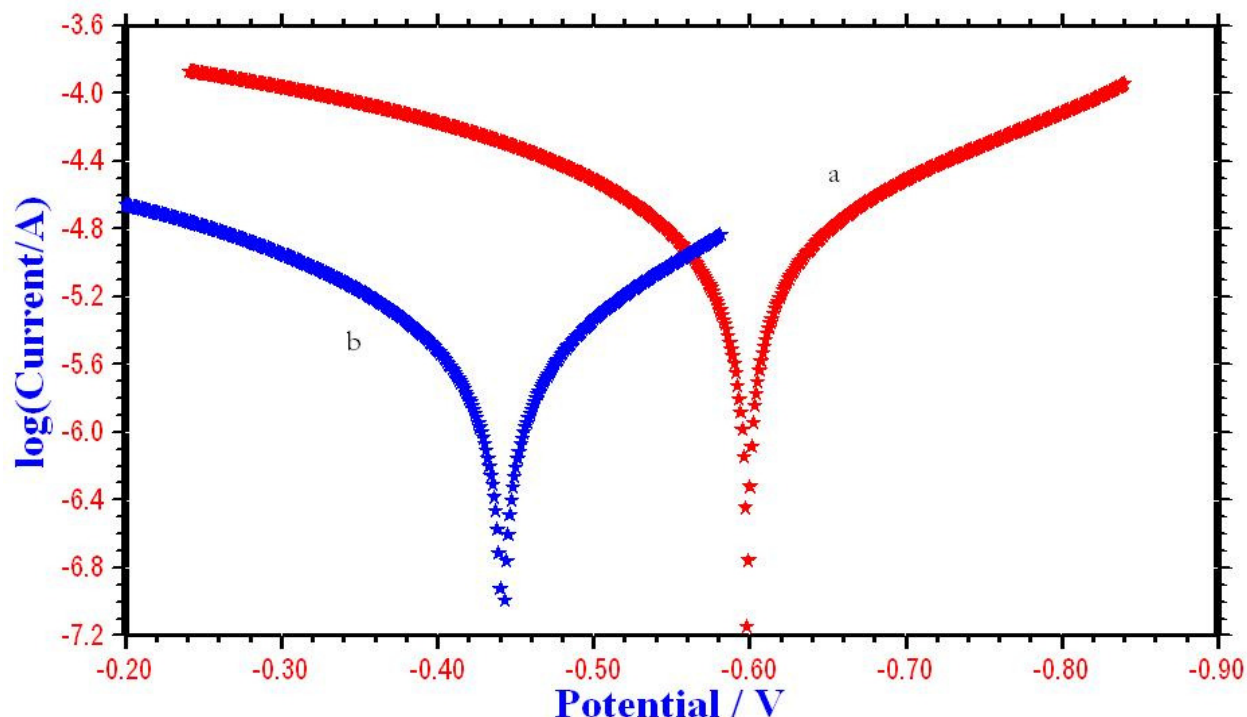

Figure-4
Potentiodynamic polarization curves of carbon steel immersed in various test solutions, a) 60 ppm Cl⁻ b) 60 ppm Cl⁻ + 25 ppm DTPMP + 25 ppm ST + 10 ppm Zn²⁺

From the polarization curves the current density (i_{corr}) was determined by Tafel extrapolation method and the corrosion rates were determined from i_{corr} values. The anodic and cathodic potentiodynamic polarization curves for carbon steel in 60 ppm Cl⁻ in the absence and presence of an inhibitor is represented in figure 4. Addition of inhibitors to the test solution showed a shift in corrosion potential towards cathodic direction corresponding to the predominant control of cathodic reaction. The corrosion current was decreased considerable in the presence of inhibitor formulation. The value of Corrosion rate of carbon steel in the presence of inhibitor was much smaller than that in the absence of an inhibitor. In presence of inhibitor, the I.E was about 78 %. When Carbon steel is immersed in 60 ppm Cl⁻ environment the corrosion current I_{corr} is 1.26×10^{-5} A/cm². When 25 ppm DTPMP, 25ppm ST, 10 ppm Zn²⁺ are added the corrosion current decreases to 2.79×10^{-6} A / cm². The significant reduction in corrosion current indicates a decrease in corrosion rate in the presence of inhibitor. For the Blank system the corrosion potential is - 598 mV vs SCE, for the inhibitor

system the potential of corrosion is -0.442 mV vs SCE. This suggests this formulation controls the cathodic reaction predominantly. From the Polarization curves it can be inferred that $Zn(OH)_2$ formed[32] on the metal surface retards the oxygen reduction reaction and thus controls the cathodic reaction of the metal. The DTPMP- ST – Zn²⁺ system shifts the corrosion potential to cathodic side. Thus the ternary inhibitor formulation acts as cathodic inhibitor. This indicates the protective film formed on the metal surface.

Mechanism of Corrosion Inhibition: In order to explain the experimental results, the following mechanism was proposed for corrosion inhibition. The formulation consisting of 25 ppm of DTPMP, 25 ppm of ST and 10 ppm of Zn²⁺ has 92 % Inhibition Efficiency. Polarization study reveals that the formulation functions as cathodic 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⁻, 25 ppm DTPMP, 25 ppm ST and 10 ppm Zn^{2+} is prepared, there will be the formation of DTPMP-Zn^{2+} and ST- Fe^{2+} 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 Zn^{2+} complexes are converted into iron complexes[33] on the anodic sites.

Zn^{2+} - DTPMP + Fe^{2+} → Fe^{2+} - DTPMP + Zn^{2+}

Zn^{2+} - ST + Fe → Fe^{2+} - ST + Zn^{2+}
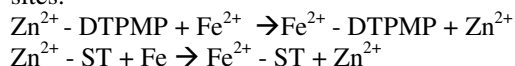
The released Zn^{2+} ions reacts with OH^- ions to form $Zn(OH)_2$

Zn^{2+} + $2OH^-$ → $Zn(OH)_2$ ↓

Thus the protective film consists of Fe^{2+} - DTPMP, Fe^{2+} - ST and $Zn(OH)_2$ complexes.

Thus $Zn(OH)_2$ precipitate may take place at cathodic sites thus decreasing the rate of further oxygen reduction.

Conclusion

A formulation consisting of DTPMP, ST 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 synergistinc role in the ST- Zn^{2+} - DTPMP system. The ternary system ST (25ppm) – Zn^{2+} (10 ppm) – DTPMP (25ppm) is effective and it gives 92 % of Inhibition Efficiency. Significant synergism was obtained by the combined application of ST- Zn^{2+}- DTPMP. The concentration of Zn^{2+} can be reduced by the addition of ST. The DTPMP is an eco-friendly and is required very low concentrations. Thus this new inhibitor formulation is more environment friendly. The inhibitor formulation acts as an cathodic inhibitor. In presence of the inhibitor, the charge transfer resistance is significantly increased. Also, the double layer capacitance of surface film reduced markedly. Both ST and DTPMP from stable complexes with metal ions in the metal surface. The protective film consists of Fe^{2+} - ST, Fe^{2+} - DTPMP and $Zn(OH)_2$.

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