 ISSN: 2277-9655
Scientific Journal Impact Factor: 3.449
(ISRA), Impact Factor: 2.114

IJESRT

INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

Surface and Electrochemical Behaviour of Carbon Steel in Neutral aqueous Environment

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Abstract

Corrosion inhibiton of Carbon Steel immersed in 60 ppm Cl^- has been investigated in presence and absence of Zn^{2+} ions. The Weight – loss method is used to find the Inhibition Efficiency of the inhibitors. The formulation consists of 50 ppm of DTPMP, 10 ppm of Sodium Molybdate (SM), 10 ppm Zn^{2+} and it gives the maximum IE of 90%. When inhibitors used alone that gives some IE. But their combination in particular proportion shows the maximum IE is otherwise called as Synergistic Effect. The Electrochemical impedance spectroscopy (EIS) indicates that the formation of protective film on the surface of metal. The Atomic Force Microscopy also confirms the formation of film by the way of increasing in smoothness of the surface of Carbon Steel.

Keywords: AFM, EIS spectra, DTPMP, Carbon Steel, Neutral Environment, Sodium Molybdate

Introduction

((Diethylenetriamine penta(methylene phosphonic acid (DTPMP) along with SM and Zn^{2+} system used as an effective corrosion inhibitors for Carbon Steel in 60 ppm Cl^- . Water may be used as a good coolant in cooling water system. If the cooling water is ultra pure, then no problem due to corrosion. If it may contains impurities like dissolved gases, acids, hardness producing salts which causes corrosion to metals. Many Phosphonic acids have been used as a corrosion inhibitors such as ATMP [1,2], HEDP [3], DTPMPA[4,5]. DTPMP along with Zn^{2+} [6] used as a effective corrosion inhibitor in cooling water system.

Materials and methods

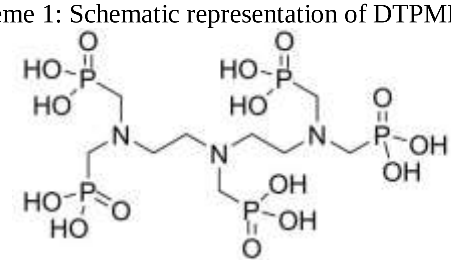
Preparation of Carbon Steel specimen

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^-.

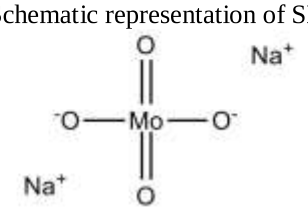
PREPARATION OF SOLUTIONS: Sodium salt of Phosphonic acid (DTPMP)

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 DTPMP

Scheme 1: Schematic representation of DTPMP



Scheme 2: Schematic representation of SM



Sodium Molybdate (SM) Solution

0.5 g of SM 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 Molybdate.

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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 Zn^{2+} ion concentration.

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 [7]. Then Weight – loss determined in order to calculate the Inhibition Efficiency and Corrosion Rate (CR) using the following formulae.

$$IE = \frac{W_o - W_i}{W_o} \times 100$$

Where,

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

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

D – Density of the metal specimen (g/cm^3), A – Area of the specimen in in^2, T – Immersion time in Hours

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.

ELECTROCHEMICAL STUDIES

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 (Rct) and Double layer Capacitance (Cdl) value were measured using the following relation.

$$Cdl = \frac{1}{2 \Pi \, Rct \, fmax}$$

SURFACE EXAMINATION STUDIES

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.

Scanning Electron Microscope (SEM)

Surface analysis was carried out using Scanning Electron Microscope (SEM). The Carbon steel specimens were immersed in 60 ppm Cl^- solution without and with inhibitor for about 1 day. After one day, immersed specimens were taken out from the test solution, cleaned with double distilled water and dried at room temperature. A SEM [8,9] experiment was performed by using a model JSM 6390 Scanning Electron Microscope.

AFM Analysis

The Carbon steel specimens immersed in various test solutions for 1 day were taken out, rinsed with double distilled water, dried and subjected to the surface examination. The surface morphology AFM [10] measurement of Carbon Steel surface was analyzed by XIE-Instrument atomic force microscopy.

Results and discussion

Weight-loss method

The inhibition efficiency (IE) of Sodium Molybdate (SM) in controlling corrosion of carbon steel immersed in 60 ppm Cl^- for a period of 3 days in the absence and the presence of Zn^{2+} is also given in Table.1. SM alone shows some IE, Whereas Zn^{2+} alone has some IE. When SM is combined with Zn^{2+} ions, it is found that the IE increases. 10 ppm SM has only 26 % IE and 10 ppm Zn^{2+} has only 24 % . But their combination shows 30 % IE. This suggests a synergistic effect between the binary inhibitor formulation SM and Zn^{2+}, SM is able to transport Zn^{2+} towards the metal surface. When 50 ppm of DTPMP is added to the inhibitor formulation is increases the IE progressively upto a certain limit. After that the IE decreases, this is because of the continuous attack of Chloride ions from the solution. The ternary inhibitor system shows the maximum IE of 90% which is shown in Table.1

Table. 1 – The Corrosion Rate and Inhibition Efficiency of Carbon Steel immersed in Neutral aqueous Environment

SMB ppm	Zn^{2+} ppm	DTPMP ppm	Corrosion Rate (mpy)	IE %
10	0	0	1.29	26
0	10	0	1.34	24
0	0	50	1.36	22
10	10	0	1.22	30
0	10	50	1.03	41
10	10	10	0.89	49
10	10	25	0.58	67
10	**10**	**50**	**0.16**	**90**

10	10	75	0.33	82
10	10	100	0.40	77

Synergism Parameter

The values of synergism parameters are shown in Table 2. 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), which is otherwise called as Antogonistic Effect.

Table 2. Synergism Parameters of Carbon Steel immersed in 60 ppm Cl^- in presence and absence of inhibitors

SM $+Zn^{2+}$ (I_2) IE %	DTPMP (I_1) IE %	SMB-Zn^{2+} - DTPMP (I'_{1+2}) IE %	SI
30	15	49	8.45
30	25	67	10.54
30	10	90	2.93
30	22	82	7.51
30	27	77	9.92

Analysis of Electrochemical Impedance Spectra (EIS)

Table - 3 EIS parameters of Carbon steel immersed in 60 ppm Cl^- Environment

S. No	Cl^- ppm	DTPMP ppm	SM ppm	Zn^{2+} ppm	R_t Ω cm^2	C_{dl} μF / cm^2	IE %
1	60	0	0	0	215	6.22×10^{-6}	----
2	60	50	10	10	3035	3.19×10^{-8}	93

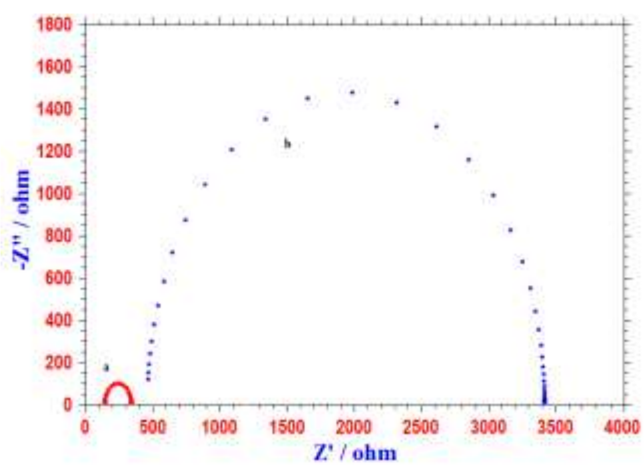


Fig.1. EIS Curves of Carbon Steel immersed in various test solutions

a) 60 ppm Cl^-
b) 60 ppm Cl^- + 50 ppm DTPMP + 10 ppm SM + 10 ppm Zn^{2+}

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 cm^2, for inhibited solution containing 50 ppm DTPMP, 10 ppm SM and 10 ppm Zn^{2+} the charge transfer resistance 3035 ohm cm^2. At the same time the double layer capacitance (C_{dl}) value getting decreases from 6.22×10^{-6}μF / cm^2 to 3.19×10^{-8} μF / cm^2. 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 [11,12]. 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 93 % inhibition efficiency. Thus the EIS spectral data reveal that a protective film is formed on the metal surface.

Analysis of Atomic Force Microscopy (AFM)

Atomic force microscopy is the powerful technique to collect the roughness statistics from the variety of surfaces. All AFM images were taken using XEI instruments 5 x 5 micrometer and 10 x 10 micrometer areas with the scan rate of 0.45 Hz.

The 2 – Dimensional and 3 – Dimensional AFM morphologies are taken for polished Carbon Steel, metal immersed in the corrosive environment and Inhibitor system which is shown in Fig. 2 a,b,c and Fig. 2 d,e,f respectively.

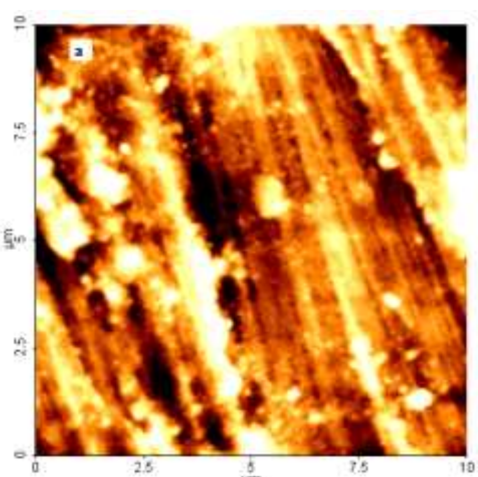
AFM analysis performed to get the values of Ra (Average Roughness), R_{RMS} (Root Meen Square Roughness) and P-V height (Peak to Valley) height. The slight roughness observed on the polised Carbon steel surface due to atmospheric Corrosion. The Ra, R RMS and P-V height values are given 19.19 nm , 24.81 nm and 166.80 nm respectively. The Ra, R RMS and P-V height values for the Carbon steel

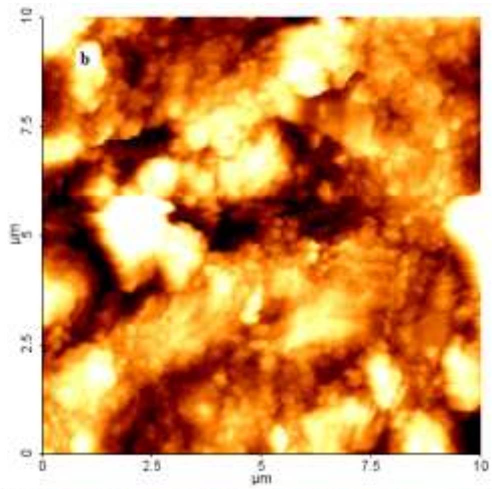
ISSN: 2277-9655
Scientific Journal Impact Factor: 3.449
(ISRA), Impact Factor: 2.114

immersed in 60 ppm Cl^- are given 144.04 nm, 182.38 nm and 742.21 nm. These values suggests that the Average roughness, Root Mean Square Roughness and Peak to Valley heights are increases due to the Corrosion of Carbon Steel in 60 ppm Cl^-. This indicates the surface becomes more rough when compared to the polished Carbon steel due to the attack of Chloride ions from the solution. The presence of 50 ppm DTPMP, 10 ppm SM and 10 ppm Zn^{2+} reduces the Ra value from 144.04 nm to 58.79 nm. R_{RMS} value significantly reduces from 182.38 nm to 86.41 nm and P-V values are also reduces from 742.21 nm to 440.87 nm. These parameters confirmed that the surface appear smoother. The smoothness of the surface is due to the formation of protective film of Fe^{2+} - DTPMP and $Zn(OH)_2$ Complex.

Table.3.AFM datas for Carbon Steel surface immersed in different Environments

Samples	Avg. Roughness Ra (nm)	Root Mean Square Roughness R_{RMS} (nm)	Maximum Peak to Valley height P-V (nm)
Polished Carbon Steel (Control)	19.19	24.81	166.80
Carbon Steel immersed in 60 ppm Cl^- (Blank)	144.04	182.38	742.21
Carbon Steel immersed in 50 ppm DTPMP + 10 ppm SM + 10 ppm Zn^{2+} (Inhibitor)	58.79	86.41	440.87





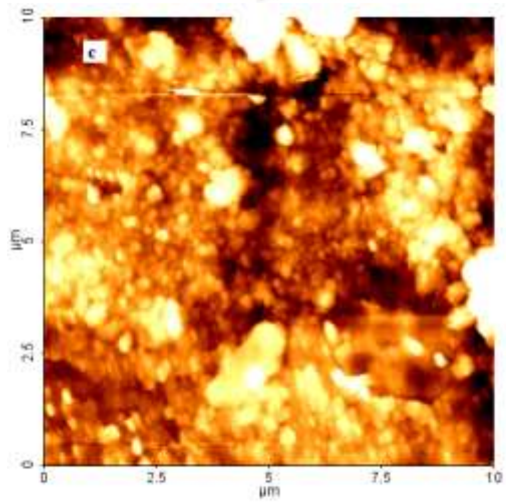
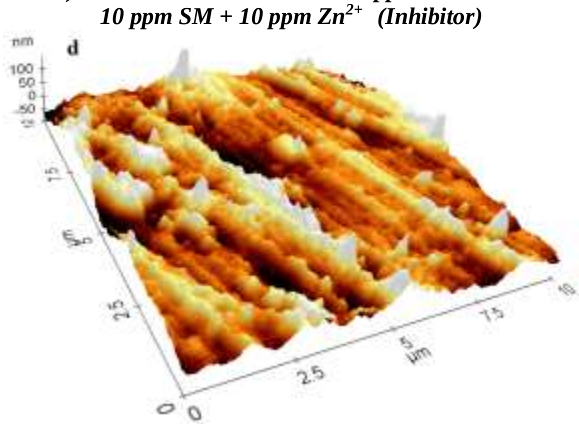


Fig.2. 2D AFM Images for Carbon Steel Surface
a) Polished Carbon Steel (Control)
b) Carbon Steel immersed in 60 ppm Cl^- (Blank)
c) Carbon Steel immersed in 50 ppm DTPMP + 10 ppm SM + 10 ppm Zn^{2+} (Inhibitor)



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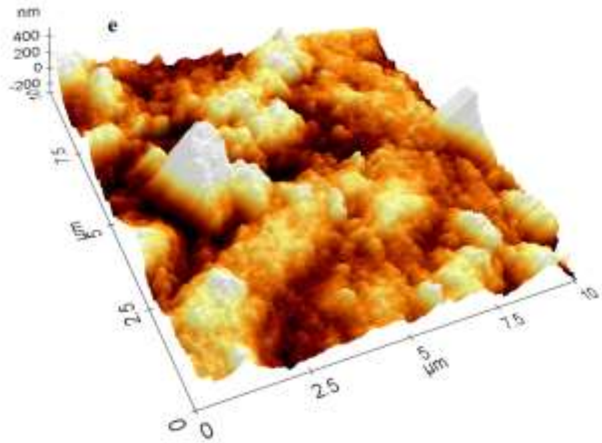

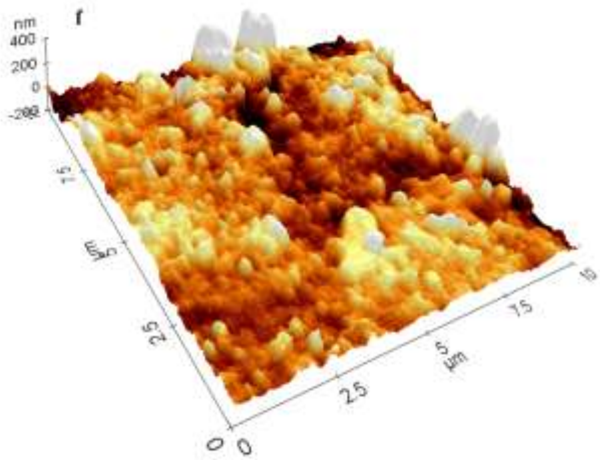

Fig.2 . 3D AFM Images for Carbon Steel surface
d) Polished Carbon Steel (Control)
e) Carbon Steel immersed in 60 ppm Cl^- (Blank)
f) Carbon Steel immersed in 50 ppm DTPMP + 10 ppm SM + 10 ppm Zn^{2+} (Inhibitor)

Conclusion

1. The DTPMP used as a good Corrosion inhibitor for Carbon Steel in neutral aqueous environment by weight – loss method.
2. The combination of 50 ppm DTPMP + 10 ppm SM + 10 ppm Zn^{2+} gives the maximum IE of 90%. This indicates that the synergistic effect is offered between the inhibitors.
3. The EIS spectra indicates that the protective film is formed on the surfac.
4. The AFM morphologies confirm the surface becomes smooth. This also confirms the formation of protectivel film on Carbon Steel.

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ISSN: 2277-9655
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