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Scientific paper
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Analysis of nano film by atomic force microscopy

The corrosion inhibition efficiency of diethylenetriaminepenta(methylenephosphonic acid) (DTPMP) in combination with a bivalent cation like Zn^{2+} in controlling corrosion of mild steel immersed in rain water collected from rooftop, stored in concrete tank was investigated using weight loss method and electrochemical impedance spectroscopy. The combined corrosion inhibition efficiency offered by 50 ppm of DTPMP and 5 ppm of Zn^{2+} was 90 %. The synergistic effect of the inhibiting compound was calculated. The corrosion inhibition was observed due to the formation of more stable and compact protective film on the metal surface. Fluorescence spectral analysis was used in detecting the presence of an iron – inhibitor complex and the co-ordination sites of the metal inhibitor with iron were determined by the FTIR spectra. The surface morphology of the protective film on the metal surface was characterized by using atomic force microscopy (AFM).

***Key words:** Synergistic effect, corrosion inhibition, mild steel, surface morphology, atomic force microscopy, fluorescence spectra, nano film*

INTRODUCTION

Inhibition of corrosion and scaling can be done by the application of inhibitors. It is noted that the effect of corrosion inhibitors is always caused by change in the state of surface being protected due to adsorption or formation of hardly soluble compounds with metal cations. Several phosphonic acids have been used as corrosion inhibitor along with metal cation such as Zn^{2+} [1-5]. Phosphonic acids are the inhibitors which have been widely used, due to their stability, ability to form complexes with metal cations and scale inhibiting properties [6-8]. Electrochemical techniques have been used in corrosion inhibition studies of mild steel by phosphonic acids [9-10]. Electrochemical techniques have provided only macroscopic details of the redox reaction and no mechanistic information [11-13]. To understand the mechanism of the effect of inhibitors on the metal surface for surface analytical techniques must be used [14, 15]. The aim of the present study was to investigate synergistic corrosion inhibition for the DTPMP and Zn^{2+} combination to mild steel immersed in rain water collected from rooftop and stored in concrete tank. The corrosion inhibition efficiency was evaluated using mass loss method and the AC impedance spectra. The protective film formed on the metal surface characterized with the help of surface analytical techniques such as fluroscence spectra, Fourier Transform Infrared spe fluroscence spectra, Fourier Transform Infrared spectroscopy (FTIR) and atomic force microscopy.

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EXPERIMENTAL

Preparation of the mild steel specimens

Mild steel specimens were chosen from the same sheet of the following composition 0.1 per cent C, 0.026 per cent S, 0.06 per cent P, 0.4 per cent Mn and the balance Fe. Mild steel specimen of the dimensions 1.0 x 4.0 x 0.2 cm were polished to mirror finish, degreased with trichloroethylene and used for mass-loss and surface examination studies. The environment chosen is the rain water collected from rooftop and stored in concrete tank. The physico- chemical parameters of rain water is given in Table 1.

Table 1 – Physico- chemical parameters of rain water

Parameters	Value
pH	8
Conductivity	122 μmhos/cm
Chloride	0 ppm
Sulphate	0 ppm
Total hardness	20 ppm
Total Dissolved Solids	55 ppm

Determination of corrosion rate

The weighed specimen, in triplicate were suspended by means of glass hooks in 100 ml beakers containing 100 ml of rain water containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} for 7 days of immersion. After 7 days of immersion the specimens were taken out, washed in running water, dried and weighed. From the change in weights of the specimen, corrosion rates were calculated using the following relationship.

$$\text{Corrosion rate} = \frac{\text{Loss in weight (mg)}}{\text{Surface area of the specimen (dm}^2) \times \text{Period of Immersion (days)}}$$

Corrosion inhibition efficiency (IE) was then calculated using the equation:

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

Where W_1 = corrosion rate in the absence of the inhibitor and W_2 = corrosion rate in the presence of the inhibitor

AC impedance measurements

EG and G electrochemical impedance analyzer model 6310 was used to record AC impedance measurements. A three – electrode cell assembly was used. The working electrode was a rectangular specimen of mild steel with one face of the electrode of constant 1 cm^2 area exposed. A rectangular platinum foil was used as the counter electrodes. A time interval of 5 to 10 min was given for the system to attain a steady state open circuit potential. Then over this steady state potential, an A.C. potential of 10 mV was superimposed. The AC frequency was varied from 100 MHz to 100 KHz. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms for various frequencies. The R_t (charge transfer resistance) and C_{dl} (double layer capacitance) values were calculated. C_{dl} values were calculated using the following relationship.

$$C_{dl} = \frac{1}{2 \times 3.14 \times R_t \times f_{max}}$$

Surface characterization studies

The mild steel specimens were immersed in blank, as well as inhibitor solutions, for a period of one day. After 1 day, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimens was analyzed by various surface analysis techniques.

FTIR spectra

These spectra were recorded in a Perkin – Elmer 1600 spectrophotometer. The film was carefully removed, mixed thoroughly with KBr and made into pellets and the FTIR spectra were recorded.

Surface analysis by fluorescence spectroscopy

Fluorescence spectra of solutions and also the films formed on the metal surface were recorded using Jasco F – 6300 spectrofluorometer.

Atomic Force Microscopy characterization (AFM)

The mild steel specimen immersed in blank and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water, dried and subjected to the surface examination. The surface morphology measurements of the mild steel surface were carried by atomic force microscopy (AFM) using Pico SPM 2100 with the software version of Pico scan version 5.4.

RESULTS AND DISCUSSION

Weight-loss method

The inhibition efficiencies (IE) and corrosion rates of DTPMP in controlling corrosion of mild steel immersed in rain water, for a period of seven days in the presence and absence of Zn^{2+} by weight loss methods are given in Table2. DTPMP alone has some IE and Zn^{2+} alone is found to be corrosive. However the formulation consisting of 50 ppm DTPMP and 5 ppm Zn^{2+} shows 90 percent IE. Weight- loss studies reveal that DTPMP and Zn^{2+} individually showed some IE but exhibited better IE when applied in combination. This suggests that DTPMP and Zn^{2+} exhibit synergistic behaviour. The anodic reactions are retarded by the formation of Fe^{2+}-DTPMP complexes. In the presence of Zn^{2+}, the cathodic reaction is also retarded (by the formation of Zn $(OH)_2$ on the cathodic sites of the metal surface). This is confirmed by an FTIR study which reveals the presence of Fe^{2+}-DTPMP complex, and Zn $(OH)_2$ on the metal surface.

Table 2 - Inhibition efficiencies (IE %) obtained from DTPMP-Zn^{2+} systems, when mild steel immersed in rain water collected from roof top. [corrosion rate (mm/y) given in parentheses]

Inhibitor system: DTPMP + Zn^{2+}
Immersion period: 7 days.

DTPMP ppm	Inhibition efficiency (IE %)			
	Zn^{2+} (ppm)			
	0		5	
0	-	(0.0903)	-10	(0.0994)
50	10	(0.0813)	90	(0.0090)
100	27	(0.0659)	84	(0.0145)
150	38	(0.0560)	82	(0.0163)
200	45	(0.0497)	80	(0.0180)
250	50	(0.0452)	78	(0.0198)

Synergism considerations

According to studies by Gomma [16], the synergism parameter (S_I) can be calculated using the relationship given by Aramaki and Hackermann [17].

$$S_I = \frac{1 - I_{1+2}}{1 - I'_{1+2}}$$

Where: $I_{1+2} = (I_1 + I_2) - (I_1 I_2)$, I_1 = Inhibition efficiency of DTPMP, I_2 = Inhibition efficiency of Zn^{2+}, I'_{1+2} = measured inhibition efficiency for DTPMP in combination with Zn^{2+}.

The calculated values are listed in parentheses in Table 3 for different concentrations of inhibitors. S approaches 1 when no interaction between the inhibitor compounds exists. When S > 1, which points to synergistic effects. In the case of S < 1, the negative interaction of inhibitor prevails, (i.e. corrosion rate increases) [18]. From Table.3, it can be seen that the most values of S_I are greater than unity, suggesting that the phenomenon of synergism exists between DTPMP and Zn^{2+} [19, 20]. Thus, the enhancement of the inhibition efficiency caused by the addition of Zn^{2+} ions to ATMP is only due to the synergistic effect.

Table 3 - Inhibition efficiencies and Synergism parameters (given in parentheses) for various concentrations of DTPMP-Zn^{2+} systems, when mild steel immersed in rain water collected from roof top

Immersion period: 7 days.

DTPMP ppm	Zn^{2+} (ppm)	
	0	5
0	-	-10
50	10	90 (1.11)
100	27	84 (3.44)
150	38	82 (5.03)
200	45	80 (6.13)
250	50	78 (7.0)

Analysis of the results of AC impedance spectra

The AC impedance spectra of mild steel immersed in various solutions were recorded (Fig. 1). The AC impedance parameters, namely, charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in Table 4. When mild steel is immersed in rain water R_t value is 931 Ω cm^2 and C_{dl} value is 441 x 10^{-6} μF cm^{-2}. When DTPMP and Zn^{2+} are added to rain water, R_t value increases from 931 Ω cm^2 to 2306 Ω cm^2. The C_{dl} decreases from 441 x 10^{-6} μF cm^{-2} to 370 x 10^{-6} μF cm^{-2}.

Table 4 - Impedance parameters for corrosion of mild steel immersed in rain water in the presence and absence of inhibitor system (DTPMP-Zn^{2+}) obtained from AC impedance curves.

System	R_t Ω cm^2	C_{dl} μF cm^{-2}
Rain water	931	441 x 10^{-6}
Rain water + DTPMP (50 ppm) + Zn^{2+} (5 ppm)	2306	370 x 10^{-6}

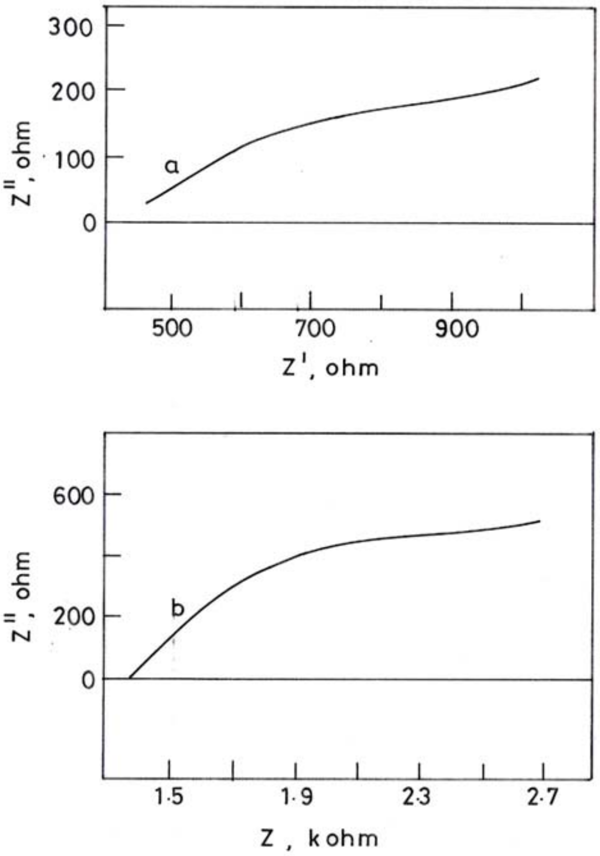


Figure 1 - AC impedance spectra of mild steel immersed in various solutions. a) Rain water collected from roof top; b) Rain water + DTPMP (50 ppm) + Zn^{2+} (5 ppm)

Analysis of the fluorescence spectra

Fluorescence spectra are useful in detecting the presence of iron-inhibitor complexes on the metal surface and also to compare the relative amounts of the complexes formed on the surface based on the intensities of the peaks [21].

The Fluorescence spectrum (λ_{ex}=225 nm) of aqueous solution containing 50 ppm DTPMP and 100 ppm Fe^{2+} (freshly prepared $FeSO_4.7H_2O$) shows peak at 326 nm (Fig. 2). The fluorescence spectrum (λ_{ex}=225 nm) of the mild steel immersed in 50 ppm Zn^{2+} and 250 ppm DTPMP is given in Fig. 2. It gave peak at 322 nm. The shift in the λ_{max} value and also increase in intensity of the peak is noticed. This indicates the formation of Fe^{2+} - DTPMP complex on the metal surface. The complex is of somewhat highly symmetric in nature, since the number of peaks obtained is only one [22]

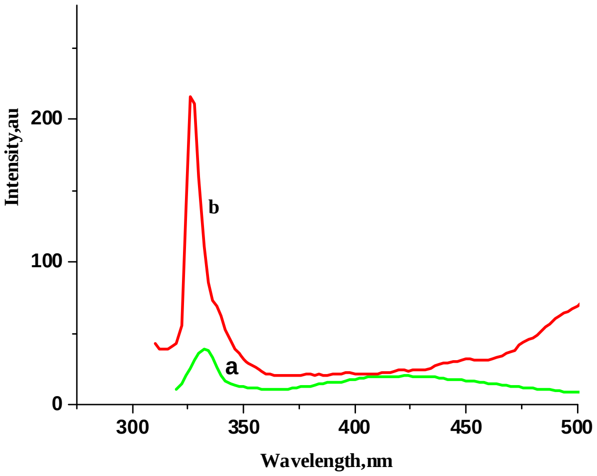


Figure 2 - Fluorescence spectra of: a) DTPMP –Fe^{2+} system; b) Mild steel surface immersed in rain water containing DTPMP (250 ppm) + Zn^{2+} (5 ppm)

Analysis of FTIR spectra

The FTIR spectrum of pure DTPMP is given in Fig. 3. The CN stretching frequency occurs at 1111 cm^{-1} and that of P-O stretching frequency appears at 1059 cm^{-1}. The FTIR spectrum of the film scratched from the surface of the metal immersed in rain water collected from rooftop, 50 ppm DTPMP and 5 ppm Zn^{2+} is given in Fig.3.b. It is seen from the spectrum that the C-N stretching frequency of DTPMP in the free state has shifted from 1111 cm^{-1} to 1116 cm^{-1} and P-O stretching frequency has shifted from 1059 cm^{-1} to 1036 cm^{-1}. These shifts indicate that the N and O atoms are coordinated to form Fe^{2+} - DTPMP complex on the anodic sites of the metal surface [23 - 25]. The band at 1350 cm^{-1} is due to Zn $(OH)_2$ [26, 27, 28, 29].

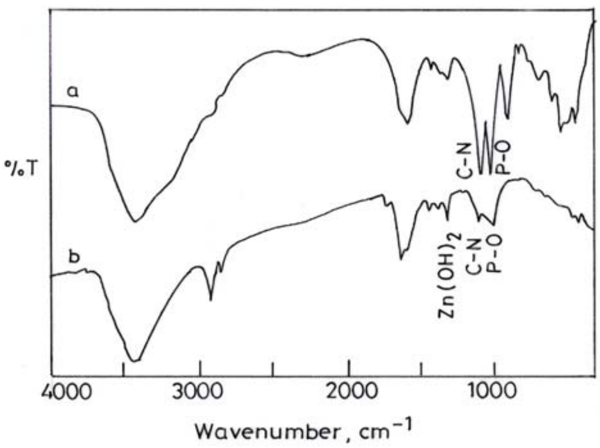


Figure 3 - FTIR spectra: a) Pure DTPMP; b) Film formed on surface of metal after immersion in rainwater + DTPMP (50 ppm) + Zn^{2+} (5ppm).

Atomic Force Microscopy Characterization

Atomic force microscopy is a powerful technique for the gathering of roughness statistics from a variety of surfaces [30]. AFM is becoming an accepted method of roughness investigation [31-35].

All atomic force microscopy images were obtained on a pico SPM 2100 AFM instrument operating in contact mode in air. The scan size of all the AFM images are 30 µm x 30 µm areas at a scan rate of 2.4 lines per second.

The two dimensional (2D), three dimensional (3D) AFM morphologies and the AFM cross-sectional profile for polished mild steel surface (reference sample), mild steel surface immersed in rain water collected from roof top (blank sample) and mild steel surface immersed in rainwater containing the formulation of 250 ppm of DTPMP and 5 ppm of Zn^{2+} are shown as Fig.4 (a, d, g), (b, e, h), (c, f, i) respectively.

Root– mean-square roughness, average roughness and peak-to-valley value

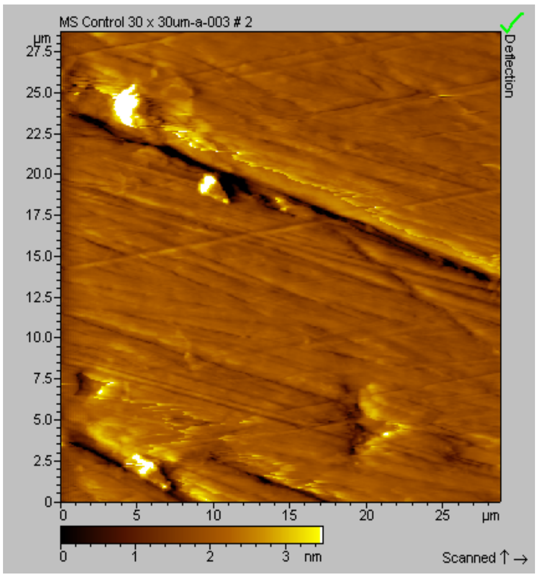
AFM image analysis was performed to obtain the average roughness, R_a (the average deviation of all points roughness profile from a mean line over the evaluation length), root-mean-square roughness, R_{RMS} (the average of the measured height deviations taken within the evaluation length and measured from the mean line) and the maximum peak-to-valley (P-V) height values (largest single peak-to-valley height in five adjoining sampling heights) [36]. R_{RMS} is much more sensitive than R_a to large and small height deviations from the mean [37].

Table 5 is summary of the average roughness (R_a), rms roughness (R_{RMS}) maximum peak-to-valley height (P-V) value for mild steel surface immersed in different environments.

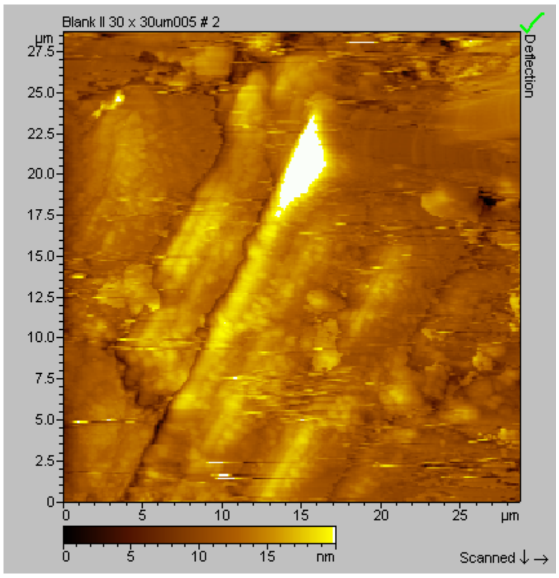
Table 5 - AFM data for mild steel surface immersed in inhibited and uninhibited environments

Samples	RMS (Rq) Roughness (nm)	Average (Ra) Roughness (nm)	Maximum peak-to-valley height (nm)
As polished mild steel(control)	265	213	1936
Mild steel immersed in rain water (blank)	897	758	3644
Mild steel immersed in rain water containing DTPMP(50ppm) and Zn^{2+} (5ppm)	537	465	2353

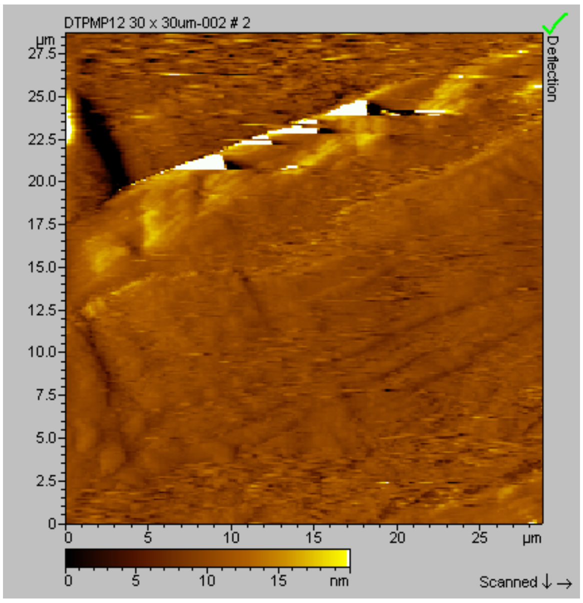
The value of R_{RMS}, R_a and P-V height for the polished mild steel surface (reference sample) are 265 nm, 213nm and 1936 nm respectively, which shows a more homogeneous surface, with some places in where the height is lower than the average depth [30]. Fig. 4 (a, d, g) displays the uncorroded metal surface. The slight roughness observed on the polished mild steel surface is due to atmospheric corrosion. The rms roughness, average roughness and P-V height values for the mild steel surface immersed in rain water are 897 nm, 758 nm and 3644 nm respectively. These data suggests that mild steel surface immersed in rain water has a greater surface roughness than the polished metal surface, which shows that the unprotected mild steel surface is rougher and was due to the corrosion of the mild steel in rainwater environment collected from rooftop. Fig. 4. (b, e, h) displays corroded metal surface with few pits.



a)

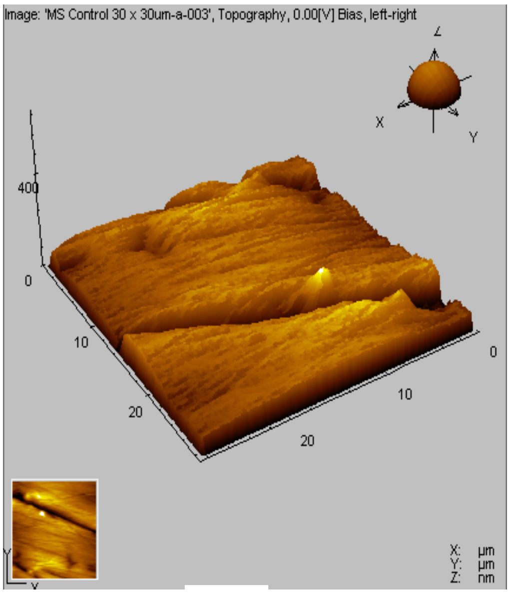


b)

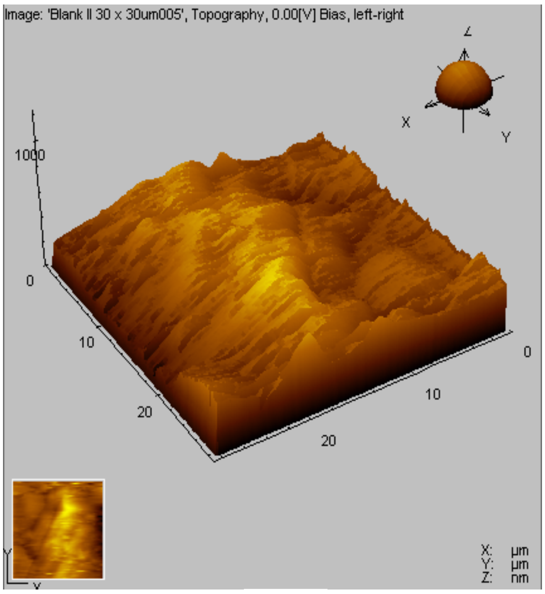


c)

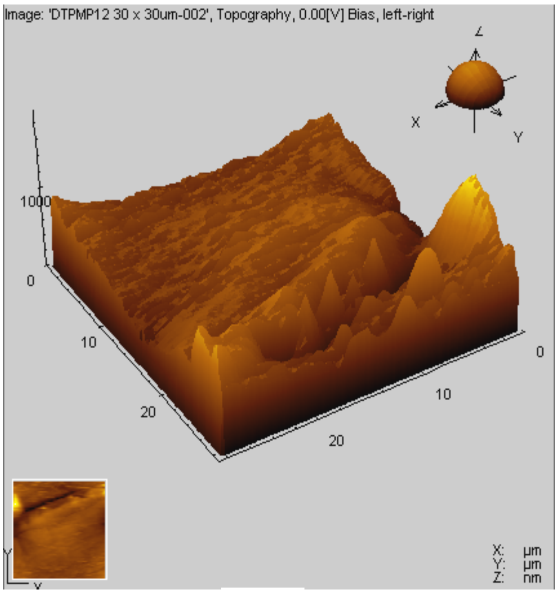
Figure 4 - 2D AFM images of the surface of: a) As polished mild steel(control); b) Mild steel immersed in rain water collected from roof top(blank); c) Mild steel immersed in rain water collected from roof top containing DTPMP (50 ppm) + Zn^{2+} (5 ppm)



d)



e)

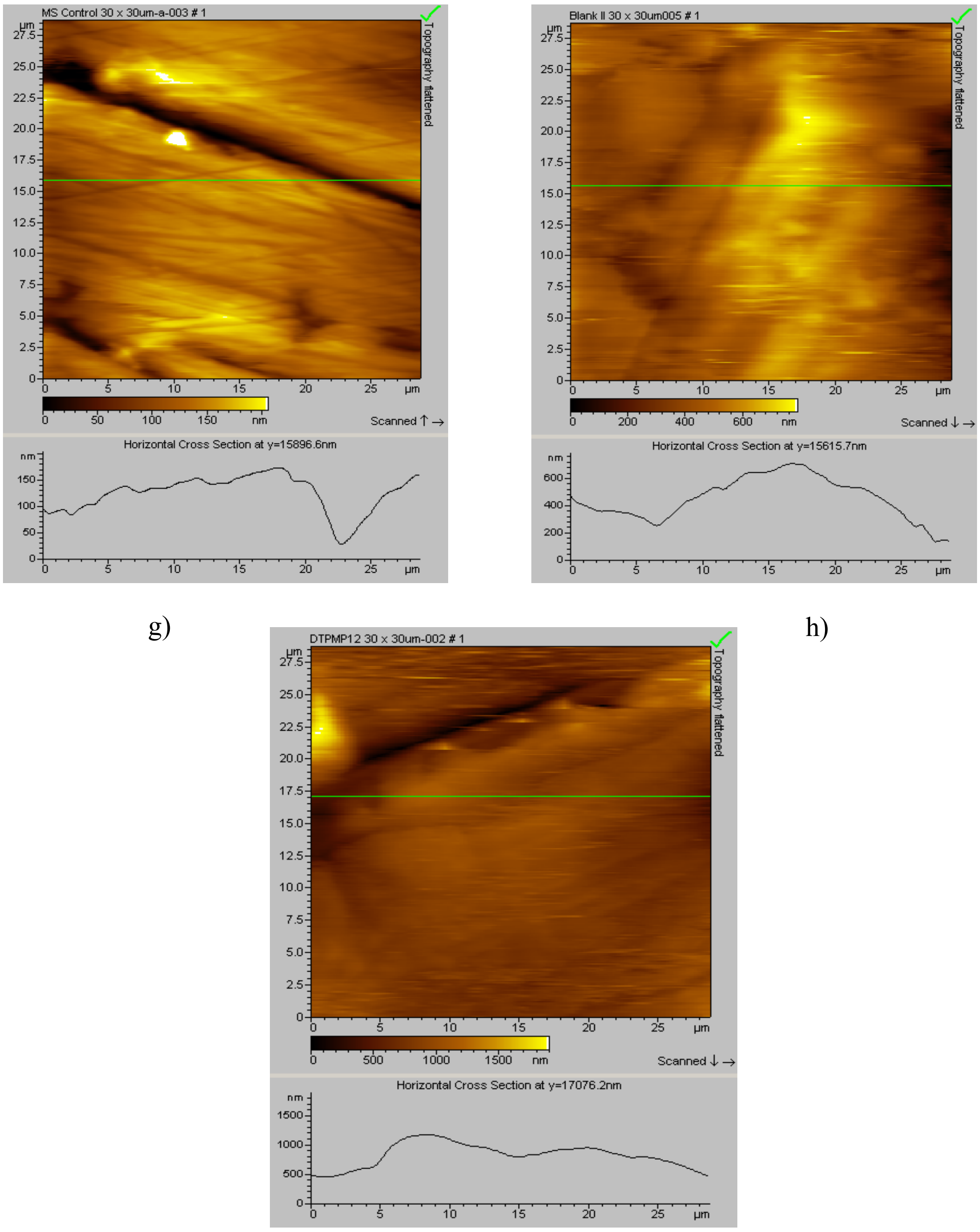


f)

Figure 4 - 3D AFM images of the surface of: d) As polished mild steel (control); e) Mild steel immersed in rain water collected from roof top (blank); f) Mild steel immersed in rain water collected from roof top containing DTPMP(50 ppm) + Zn^{2+} (5 ppm)

The presence of 50 ppm of DTPMP and 5 ppm of Zn^{2+} in the rainwater environment collected from rooftop reduces the R_{RMS} by a factor of 1.67 (537 nm) from 897 nm and the average roughness is significantly reduced to 465 nm when compared with 758 nm of mild steel surface immersed in rain water collected from rooftop. The maximum peak-to-valley height also was reduced to 2353 nm. These parameters confirm that the surface appears smoother. The smoothness of the surface is due to the formation of a compact protective film of Fe^{2+}- DTPMP complex and $Zn(OH_2)$ on the metal surface thereby inhibiting the corrosion of mild steel.

And the above parameters observed are somewhat greater than the AFM data of polished metal surface which confirms the formation of the film on the metal surface, which is protective in nature.



g) h) i)

Figure 4 - The cross-sectional profiles, which are corresponding to as Shown broken lines in AFM images of the surface of: g) As polished mild steel (control); h) Mild steel immersed in rain water collected from roof top (blank); i) Mild steel immersed in rain water collected from roof top containing DTPMP(50 ppm) + Zn^{2+} (5 ppm)

Mechanism of corrosion inhibition

The results of the weight - loss study show that the formulation consisting of 50 ppm DTPMP and 5 ppm of Zn^{2+} has 90 % IE, in controlling corrosion of mild steelin rain water. A synergistic effect exists between Zn^{2+} and DTPMP. Polarization study reveals that the formulation functions as mixed inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectral study reveals that the protective film consists of Fe^{2+} - DTPMP complex and Zn $(OH)_2$. In order to explain these facts the following mechanism of corrosion inhibition is proposed.

- When the solution containing rain water, 5 ppm of Zn^{2+} and 50 ppm of DTPMP is prepared, there is formation of Zn^{2+}-DTPMP complex in solution.
- When mild steel is immersed in this solution, the Zn^{2+}-DTPMP complex diffuses from the bulk of the solution towards metal surface.

- On the metal surface, Zn^{2+}-DTPMP complex is converted into Fe^{2+}-DTPMP complex on the anodic sites. Zn^{2+} is released
  Zn^{2+} - DTPMP + Fe^{2+} --> Fe^{2+} - DTPMP + Zn^{2+}
- The released Zn^{2+} combines with OH^- form Zn $(OH)_2$ on the cathodic sites.
  $Zn^{2+} + 2\ OH^- \longrightarrow Zn\,(OH)_2 \downarrow$
- Thus the protective film consists of Fe^{2+} - DTPMP complex and Zn $(OH)_2$.
- The SEM micrographs and AFM images confirm the formation of protective layer on the metal surface.
- The effective synergistic formulation with 50 ppm of CTAB has 96% corrosion inhibition efficiency and 100% biocidal efficiency

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