A comparative study of phosphonic acids as corrosion inhibitor for carbon steel

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The inhibition effect of phosphonic acids such as amino(trimethylenephosphonic acid) (ATMP), diethylenetriaminepenta(methylenephosphonic acid) (DTPMP) and phenyl phosphonic acid (PhPA) on the corrosion of carbon steel in rain water collected from rooftop was studied by weight loss, potentiostatic polarization and electrochemical impedance spectroscopy methods. The results show that the inhibition efficiency (IE) of the phosphonic acids used were in the order of ATMP > DTPMP > PhPA in the presence of Zn^{2+}. A synergistic effect exists between the phosphonic acids and Zn^{2+}. The protective film formed on the metal surface was confirmed by FTIR spectroscopy, AFM spectra and SEM methods.

Key words: Carbon steel, Phosphonic acids, Corrosion inhibition, Synergistic effect, Electrochemical studies, Surface analysis methods.

1 Introduction

Phosphonates are molecules that contain one or more groups R-PO(OH)$_2$. Their good chemical stability and solubility in water make possible their use in the inhibition of corrosion and scale formation [1]. Among all these properties, their ability to form strong complexes with metal plays a very important role in the rate of transport of these compounds in the environment. Phosphonates are a group of chelating agents that are used in cooling water and desalination systems to inhibit scale formation and corrosion [2]. Different phosphonic acids are used in cooling water technology over

decades and the corrosion inhibition is decided by the ability to form a protective film on steel. Studies have been carried out with different phosphonic acids in different corrosive environment. The results showed the addition of these molecules decreased the corrosion current density and the corrosion rate [3-5]. The presence of Ca^{2+} and Zn^{2+} ions enhances the inhibition efficiency by synergism [6-8]. In the present study the inhibition effect of phosphonic acids such as amino(trimethylenephosphonic acid) (ATMP), diethylenetriaminepenta(methylenephosphonic acid) (DTPMP) and phenyl phosphonic acid (PhPA) on the corrosion of carbon steel in rain water collected from rooftop was studied by weight loss, potentiostatic polarization and electrochemical impedance spectroscopy methods. The results show that the inhibition efficiency (IE) of the phosphonic acids used were in the order of ATMP > DTPMP > PhPA. The synergistic effect existing between Zn^{2+} and the various phosphonic acids were also studied. The protective film formed on the metal surface was confirmed by FTIR spectra. The extent of the roughness of the metal surface in the absence and presence of inhibitors were shown by AFM. The surface morphology of the carbon steel was shown by SEM.

2   Experimental

2.1 Materials and Solutions

2.1.1 Preparation of the carbon specimens

The carbon steel specimens were chosen from the same sheet of the following composition: Carbon - 0.1 per cent, Sulphur - 0.026 per cent, phosphorus - 0.06 per cent, Manganese - 0.4 per cent and the balance iron. Carbon 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 weight - loss and surface examination studies.

2.1.2 Inhibitors and Solutions

The molecular structure of inhibitors used are shown in the Fig. 1
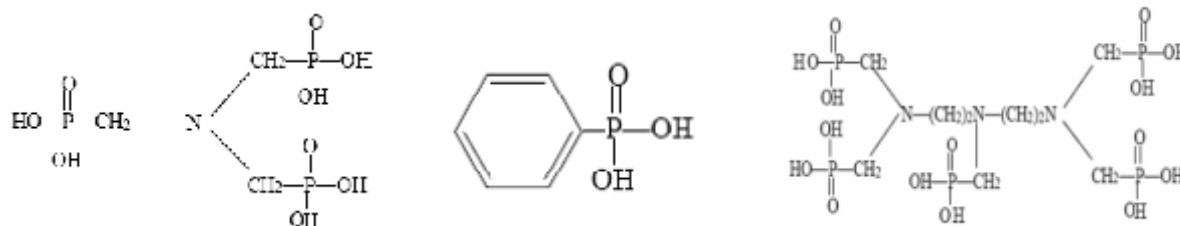
Fig 1   ATMP   PhPA   DTPMP

All the inhibitor solutions are prepared by neutralising and made with distilled water. The environment chosen is the rain water collected from roof top and stored in concrete tank. The physico- chemical parameters of rain water is given in Table 1.

2.2 Determination of corrosion rate

2.2.1 Weight loss method

The weights of the specimens before and after immersion were determined using a balance, Shimadzu AY62 model. 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.

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

Corrosion rate in mm/y = 0.004638 x mdd

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.

The inhibition efficiencies (IE) of various concentrations of phosphonic acids in controlling corrosion of carbon steel immersed in rain water, for a period of seven days in the presence and absence of Zn^{2+} by weight loss methods and the corresponding corrosion rates (CR) in mm/y are given in Table.2.

2.2.2 Synergism considerations

According to studies by Gomma [9], the synergism parameter (SI) can be calculated using the relationship given by Aramaki and Hackermann [10].

$$S_I = \frac{1-\theta_{1+2}}{1-\theta'_{1+2}}$$

Where

$\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \theta_2),$

θ_1 = Surface coverage by phosphonates

θ_2 = Surface coverage by Zn^{2+}

θ'_{1+2} = Measured surface coverage by both phosphonates and Zn^{2+}

Let the surface coverage be represented by θ; θ = % IE/ 100

The calculated values are listed in Table 3 for different concentrations of inhibitors. S_I approaches 1 when no interaction between the inhibitor compounds exists. When $S_I > 1$, which points to synergistic effects. In the case of $S_I < 1$, the negative interaction of inhibitor prevails, (i.e. corrosion rate increases) [11]. From Table 3, it can be seen that the most values of S_I is greater than unity, suggesting that the phenomenon of synergism existing between phosphonates and Zn^{2+} [12, 13]. Thus, the enhancement of the inhibition efficiency caused by the addition of Zn^{2+} ions to phosphonates is only due to the synergistic effect.

2.2.3. Potentiostatic polarization study

This study was carried out using EG and G electrochemical impedance analyzer model 6310. A three – electrode cell assembly was used. The working electrode was used as a rectangular specimen of carbon steel with one face of the electrode of constant 1 cm^2 area exposed. A saturated calomel electrode (SCE) was used as reference electrode. 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. The results such as Tafel slopes, I_{corr} and E_{corr} values were calculated. The working electrode and platinum electrode were immersed in rain water in the absence and presence of inhibitor. Saturated calomel electrode was connected with the test solution through a salt bridge. Potential (E) vs. log current (I) plots were then recorded. Corrosion potential (E_{corr}) and Tafel slopes b_a and b_c were determined from E vs. log I plots. Tangents were drawn on the cathodic and anodic polarization curves. From the point of intersection of the two tangents I_{corr} and E_{corr} were calculated. The inhibition efficiency (IE) is calculated from the following equation,

$$I.E\ (\%) = [(I_{corr} - I^*_{corr} / I_{corr})]\ x\ 100$$

Where I_{corr} and I^*_{corr} are current densities without and with inhibitor respectively.

The corrosion parameters of carbon steel immersed in various test solutions obtained by polarization study are given in Table 4. The polarization curves are shown in Fig 2. When carbon steel is immersed in rain water collected from roof top, the corrosion potential is -710 mV vs. saturated calomel electrode (SCE). It is observed from Table 4 that the corrosion potential for all the inhibitor system shifts to the anodic (noble) direction when compared with that of E_{corr} of blank -710 mV vs SCE. This suggests that the anodic reaction is controlled predominantly indicating that the dissolution of the metal is reduced, since more phosphonic acids is transported to the anodic sites in the presence of Zn^{2+}.

The current of the iron dissolution decreased significantly, indicating that the metal surface was passivated by the formed inhibitor layer. The passivity of iron is probably due to the formation of a Fe^{2+} – phosphonic acids surface layer. It was discussed in the literature [14] that the anodic action of phosphonic acids is mainly based on the formation of insoluble complexes at the anodic sites of the metal surface. This indicates that a protective film is formed on the metal surface.

2.2.4. AC impedance measurements

EG and G electrochemical impedance analyzer model 6310 was used to record AC impedance measurements. The cell set up was the same as that used for polarization measurements. 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 kHz to 100 mHz. 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.

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

The inhibition efficiency (IE) is calculated from the following equation,

$$I.E\ (\%) = [(1/R^*_t - 1/R_t) / 1/R^*_t] \times 100$$

Where R^*_t and R_t are the charge transfer resistance without and with inhibitors, respectively

The AC impedance spectra of carbon steel immersed in various solutions were recorded. (Fig. 3). The AC impedance parameters, namely, charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in Table 4. When carbon 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}. From the Table 4, it is inferred that the charge transfer resistance (R_t) value of the inhibitor increases tremendously from that of the blank. Also, the double layer

capacitance (C_{dl}) decreases when compared with the C_{dl} value of the blank. This suggests that a protective film is formed on the surface of the metal. The greater decrease in the R_t value, among the phosphonates is found for ATMP- Zn^{2+} system. This accounts for the very high IE of ATMP- Zn^{2+} system.

2.3. Surface characterization studies

The nature of the film formed on the surface of the metal specimens was analyzed by various surface analysis techniques.

2.3.1 Scanning Electron Microscopic studies (SEM)

The carbon 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 observed in a scanning electron microscope to examine the surface morphology. The surface morphology measurements of the carbon steel were examined using Hitachi S-3000 H computer controlled scanning electron microscope.

2.3.2 Atomic Force Microscopy characterization (AFM)

The carbon 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 carbon steel surface were carried by atomic force microscopy (AFM) using PicoSPM 2100 with the software version of Picoscan version 5.

2.3.3 FTIR spectra

These spectra were recorded in a Perkin – Elmer 1600 spectrophotometer with a resolving power of 4 cm^{-1}. The film was carefully removed, mixed thoroughly with KBr and made into pellets and the FTIR spectra were recorded after the immersion period of 1 day in various environments.

3   Results and Discussion

The percentage inhibition efficiency of the various inhibitor formulations in controlling corrosion of carbon steel immersed in rain water collected from rooftop obtained by weight loss method, polarization method and impedance method are shown in Table 6.

The corrosion inhibition efficiency of the phosphonic acids used is in the order of ATMP > DTPMP > PhPA. The interactions of inhibition with metal surfaces have been discussed in relation to Pearson [15] concept of 'hard-soft acids and bases'. In neutral solutions, the ferric and ferrous in the oxide films, as hard acids; tend to form ionic bonds with hard bases particularly those containing oxygen. Thus compounds which are strongly adsorbed and act as inhibitors on oxide covered iron surfaces are mainly oxygen containing anions such as hydroxide, phosphate, phosphonate, carboxylate and borate. In the present study, maximum inhibition efficiencies are shown by phosphonates as these are the hard bases which tend to adsorb on the metal surface, whose oxide films are hard acids. The number of phosphonate group affects adsorption on to the metal surface. Maximum extent of adsorption continues to decrease as the number of phosphonate group increases. When total phosphonate concentration is high, the higher fraction of surface sites occupied and the negative charge deposition on the surface through phosphonate adsorption disfavour adsorption of additional phosphonate molecules [16]. Thus ATMP shows better inhibition efficiency than DTPMP. Prevention of corrosion also depends on the surface coverage by the molecule. Mono functional compound covers low surface area per molecule and difunctional compound covers large surface area per molecule [17]. Hence in ATMP due to presence of three phosphonic groups (seven coordination sites) the concentration of ATMP required for better inhibition will be high, i.e., 250 ppm of ATMP shows 98 % of IE with 5 ppm of Zn^{2+} and DTPMP thus shows maximum of 90% IE even with 50 ppm. PhPA shows less IE due to the bulk precipitation of a Zn^{2+} - PhPA complex and thus leads to a loss of active

inhibitor to precipitation, leading to insufficient levels to adhere on to the metal surface and to form protective film.

Inhibition efficiencies derived from impedance data have been compared with those obtained from polarization and weight loss measurements. The inhibition effect obtained by impedance method is much smaller than in the case of weight loss experiment or polarization study. Weight loss method is an average method. The duration of immersion is high (7 days). During this long period of immersion the protective film formed is strengthened and the film becomes more compact. The inhibition efficiencies obtained from weight loss method and polarization study are very close to each other. However it is interesting to note that the inhibition efficiencies obtained from AC impedance spectra are lower. A probable reason for this observation may be that during the instantaneous study of AC impedance spectra, the film formed on the metal surface is porous and amorphous. There is no time lag for strengthening of the film, so the film is broken within the short period and hence low inhibition efficiency is observed during the AC impedance spectral study.

Synergism consideration

It has been observed that zinc salts markedly increases cathodic polarization. Their action is generally attributed to the precipitation of zinc hydroxide on the cathodic areas as a result of locally elevated pH [18, 11]. Hence zinc is the most commonly used cathodic inhibitor because zinc is very popular since it forms the film very rapidly but it is never used alone, due to its poor durability of the film and its tendency to precipitate at above pH 8.

In the present study the corrosion rate of carbon steel immersed in rain water collected from rooftop increases in presence of $ZnSO_4$. In case of phosphonic acids discussed, there exists maximum synergism with lower concentrations of Zn^{2+} ions. The optimum concentration of ATMP and Zn^{2+} ion for maximum synergistic effect is 250 ppm and 5 ppm respectively. The molar ratio of ATMP with

Zn^{2+} is 50:1. The optimum concentration of DTPMP and Zn^{2+} ion is 50 ppm and 5 ppm respectively.

The molar ratio of DTPMP with Zn^{2+} is 10:1. The molar ratio of PhPA with Zn^{2+} is 2:1.

SEM Analysis of Metal Surface

SEM provides a pictorial representation of the surface. To understand the nature of the surface film in the absence and presence of inhibitors and the extent of corrosion of carbon steel, the SEM micrographs of the surface are examined. The SEM images of magnification (X1000) of carbon steel specimen immersed in the rainwater for 1 day in the absence and presence of inhibitor system are shown in Fig.4(b) and Fig.4(c, d, e) respectively. The SEM micrographs of polished carbon steel surface (control) in Fig 4(a) shows the smooth surface of the metal. This shows the absence of any corrosion products or inhibitor complex formed on the metal surface.

The SEM micrographs of carbon steel surface immersed in rainwater in Fig 4(b) showed the roughness of the metal surface which indicates the corrosion of carbon steel in rainwater. Fig.4 (c, d, e) shows the inhibitor film that indicates the effect of inhibitor system on the metal surface. These images suggest that in the presence of ATMP, DTPMP along with Zn^{2+} inhibitor system the surface is covered by a thin layer of inhibitors which effectively controls the dissolution of carbon steel. The less compact and less smoothness of the surface is due to the poor inhibition nature of phenylphosphonic acid in combination with Zn^{2+}.

Atomic Force Microscopy Characterization

Atomic force microscopy is a powerful technique for the gathering of roughness statistics from a variety of surfaces [19]. AFM is becoming an accepted method of roughness investigation [20, 21].

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 three dimensional (3D) AFM morphologies for polished carbon steel

surface (reference sample), carbon steel surface immersed in rain water collected from rooftop (blank sample) and carbon steel surface immersed in various environments are shown as Fig 5 (a), (b), (c, d, e) 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_q (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) [22]. R_q is much more sensitive than R_a to large and small height deviations from the mean [23].

Table 5 is summary of the average roughness (R_a), rms roughness (R_q) and maximum peak-to-valley height (P-V) value for carbon steel surface immersed in different environments.

The value of R_q, R_a and P-V height for the polished carbon 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 [19]. Fig 5 (a) displays the uncorroded metal surface. The slight roughness observed on the polished carbon steel surface is due to atmospheric corrosion. The rms roughness, average roughness and P-V height values for the carbon steel surface immersed in rain water are 897 nm, 758 nm and 3644 nm respectively. These data suggests that carbon steel surface immersed in rain water has a greater surface roughness (as shown in Fig.5 b) than the polished metal surface, which shows that the unprotected carbon steel surface is rougher and was due to the corrosion of the carbon steel in rainwater environment collected from roof top. In presence of the phosphonic acids such as ATMP, DTPMP and PhPA as corrosion inhibitors the roughness parameters such as R_a value has been reduced from the blank value 758 nm to 323 nm, 465 nm and 590nm respectively. The R_q value was also found to be reduced from 897 nm to 396 nm, 537 nm, and

708 nm respectively) and the maximum peak- to-valley height also was reduced from the blank value 3644 nm to 2403 nm, 2353nm, 3100nm respectively. Hence the significant reduction of these roughness parameters confirms that the surface appears smoother and also provides further evidence for the phosphonic acids inhibition efficiency order as ATMP > DTPMP > PhPA. The smoothness of the surface is due to the formation of a compact protective film of Fe^{2+} - phosphonic acid complex and $Zn(OH)_2$ on the metal surface thereby inhibiting the corrosion of carbon steel. Fig.5 (c, d, e) displays the protective nature of the metal surface. Also the parameters observed for carbon steel immersed in rain water containing phosphonic acids 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.

Surfaces analysis by FTIR spectra

The FTIR spectrum of pure phosphonic acids and the FTIR spectrum of the film scratched from surface of the metal immersed in rain water collected from roof top containing the various phosphonic acids are given given in Fig 6. It is seen from the spectrum the shifts in C-N and P-O stretching frequency indicates that the N and O atoms are coordinated to form Fe^{2+} - Phosphonic acid complex on the anodic sites of the metal surface [24,25]. The band at 1350 cm^{-1} is due to $Zn(OH)_2$ [26,27].

4 Conclusion

The results of the weight - loss study show that the phosphonic acids and Zn^{2+} formulation controls corrosion of carbon steel in rain water. A synergistic effect exists between Zn^{2+} and phosphonic acids. Polarization study reveals that the formulation functions as anodic 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+} -Phosphonic acid complex and $Zn (OH)_2$.

- When the solution containing rain water, phosphonic acids and Zn^{2+} are prepared, there is formation of Zn^{2+}- phosphonic acids complex in solution.

- When carbon steel is immersed in this solution, the Zn^{2+}- phosphonic acids complex diffuses from the bulk of the solution towards metal surface.

- On the metal surface, Zn^{2+}- phosphonic acids complex is converted into Fe^{2+}- phosphonic acids complex on the anodic sites. Zn^{2+} is released

$$Zn^{2+} \text{ - phosphonic acids} + Fe^{2+} \text{ ------>} Fe^{2+} \text{ - phosphonic acids} + Zn^{2+}$$
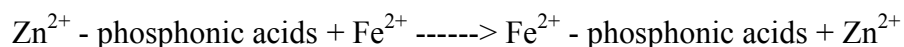
- The released Zn^{2+} combines with OH^- form $Zn(OH)_2$ on the cathodic sites.

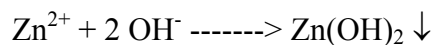$$Zn^{2+} + 2\ OH^- \text{ ------->} Zn(OH)_2 \downarrow$$

Table 1 Physico – chemical parameters of rain water collected from rooftop

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

Table 2 Inhibition efficiencies and corrosion rate in mm/y (given in parentheses) for various concentrations of Zn^{2+}- Phosphonic acids systems, when carbon steel immersed in rain water collected from rooftop. Immersion period: 7 days

Corrosion rate for carbon steel without inhibitor = 0.0903 mm/y

Inhibitor(ppm)+ Zn^{2+} (5 ppm)	Inhibition efficiency (IE %)					
	0	50	100	150	200	250
ATMP	-10 (0.0994)	40 (0.0510)	52 (0.0434)	55 (0.0407)	60 (0.0361)	98 (0.0018)
DTPMP	-10 (0.0994)	90 (0.0090)	84 (0.0145)	82 (0.0163)	80 (0.0180)	78 (0.0198)
PhPA	-10 (0.0994)	85 (0.0135)	70 (0.0271)	60 (0.0361)	46 (0.0487)	34 (0.0596)

Table 3 Synergism parameters for various concentrations of Zn^{2+}- Phosphonic acids systems, when carbon steel immersed in rain water collected from rooftop

Inhibitor (ppm) + Zn^{2+} (5 ppm)	Synergism parameters (S_I)					
	0	50	100	150	200	250
ATMP	-	1.65	1.72	1.76	1.93	35.75
DTPMP	-	10.1	5.02	3.79	3.03	2.5
PhPA	-	2.42	1.10	2.23	1.75	1.47

Table 4 Electrochemical parameters and the corresponding inhibition efficiency for the corrosion of carbon steel in rain water collected from rooftop in the presence and absence of various phosphonic acids

Inhibitor system	Polarization parameters					AC Impedance parameters		
	E_{corr} mV vs SCE	ba mV/decade	bc mV/decade	I_{corr} A/cm^2	IE %	R_t Ω cm^2	C_{dl} F cm^{-2}	IE %
Rain water	-710	270	215	3.981×10^{-5}	-	931	441×10^{-6}	-
Rain water + ATMP (250 ppm) + Zn^{2+} (5 ppm)	-548	56	57	3.162×10^{-7}	99	2229	237×10^{-6}	58
Rain water + DTPMP (50 ppm) + Zn^{2+} (5 ppm)	-540	103	103	6.723×10^{-6}	83	2306	370×10^{-6}	60
Rain water + PhPA (50 ppm) + Zn^{2+} (5 ppm)	-540	55	57	3.359×10^{-6}	92	1589	333×10^{-6}	41

Table 5 The average roughness (R_a), RMS roughness (R_q), maximum peak-to-valley height (P-V) value for carbon steel surface immersed in different environments

Samples	RMS Roughness (R_q) (nm)	Average Roughness (R_a) (nm)	Maximum peak-to-valley height (nm)
Polished carbon steel (control)	265	213	1936
Carbon steel immersed in rain water (blank)	897	758	3644
Carbon steel immersed in rain water containing ATMP(250 ppm) + Zn^{2+} (5ppm)	396	323	2402.76
Carbon steel immersed in rain water containing DTPMP(50 ppm) and Zn^{2+} (5ppm)	537	465	2353
Carbon steel immersed in rain water containing PhPA(50 ppm) and Zn^{2+} (5 ppm)	708	590	3100

Table 6 Comparison of percentage inhibition efficiencies obtained from different methods

Inhibitors system	Inhibition efficiency (IE %)		
	Using weight loss method	Using Polarization Technique	Using Impedance Technique
Rain water + ATMP (250 ppm) + Zn^{2+} (5 ppm)	98	99	58
Rain water + DTPMP (50 ppm) + Zn^{2+} (5 ppm)	90	83	60
Rain water + PhPA (50 ppm) + Zn^{2+} (5 ppm)	85	92	41

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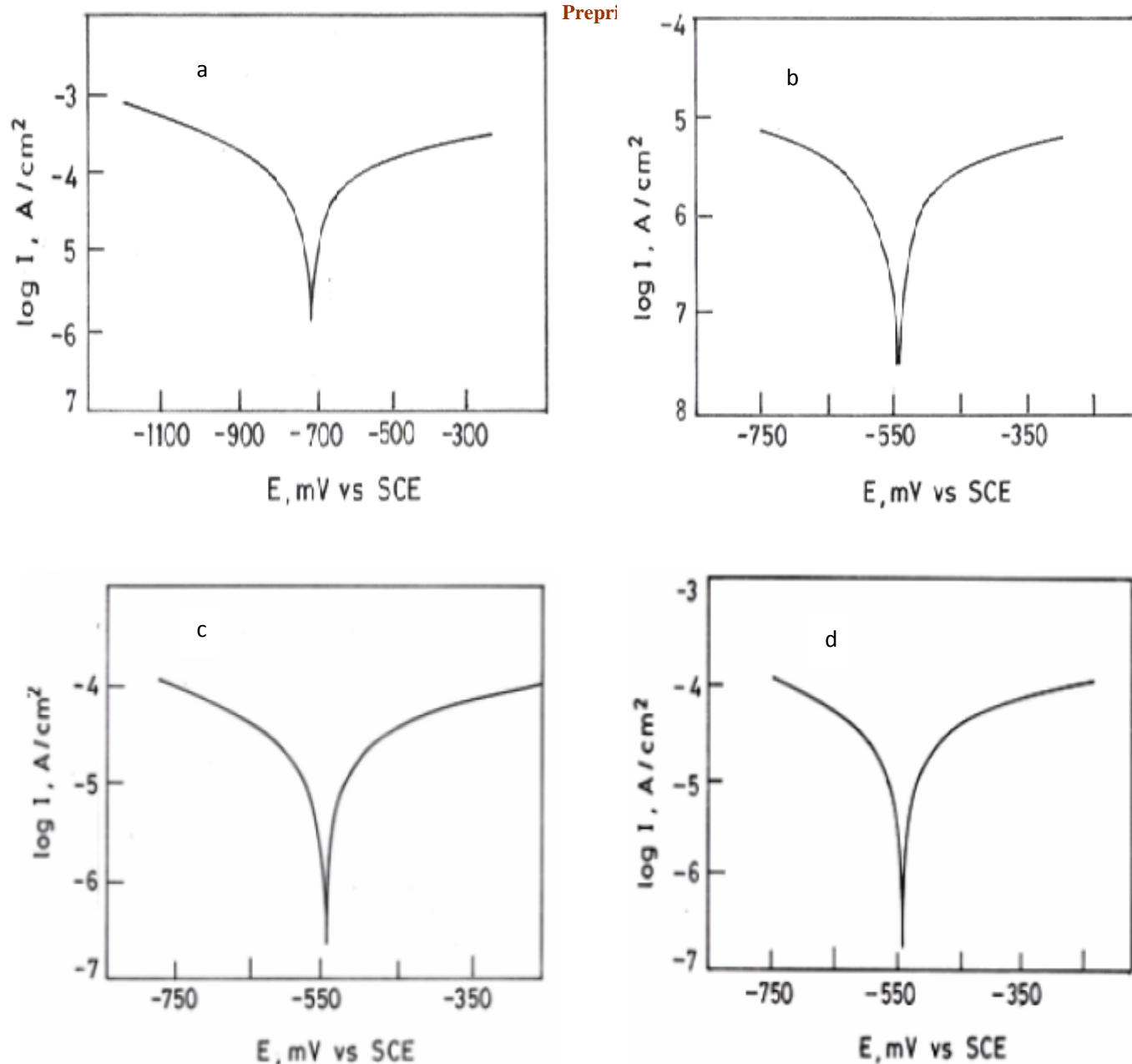
Fig 2 Polarization curves of carbon steel immersed in various solutions

a) Rain water collected from roof top

b) Rain water + ATMP (250 ppm) + Zn^{2+} (5 ppm)

c) Rain water + DTPMP (50 ppm) + Zn^{2+} (5 ppm)

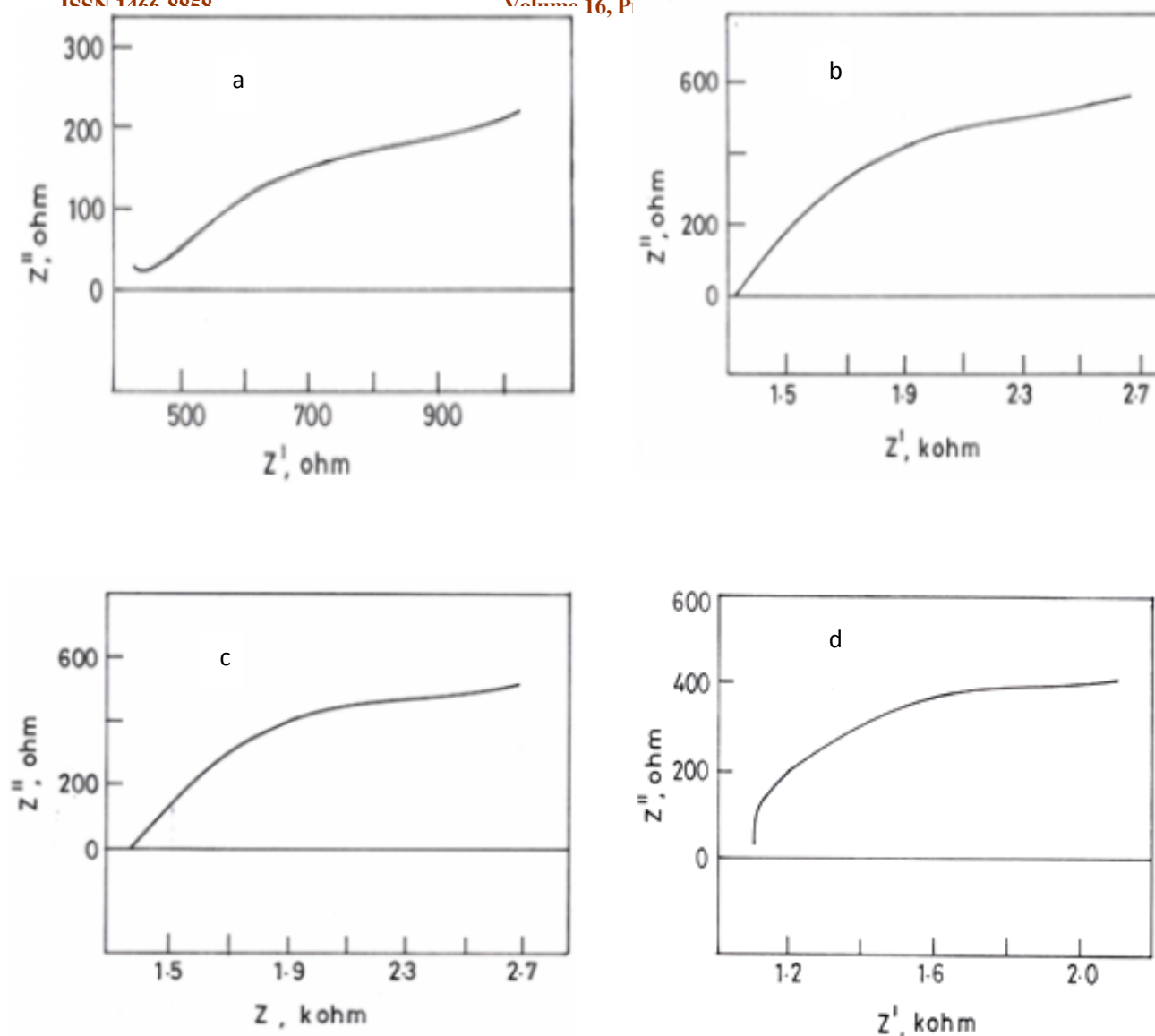d) Rain water + PhPA (50 ppm) + Zn^{2+} (5 ppm)

Fig 3   AC impedance spectra of carbon steel in

   various solutions immersed in various solutions

   a)   Rain water collected from roof top

   b)   Rain water + ATMP (250 ppm) + Zn^{2+} (5 ppm)

   c)   Rain water + DTPMP (50 ppm) + Zn^{2+} (5 ppm)
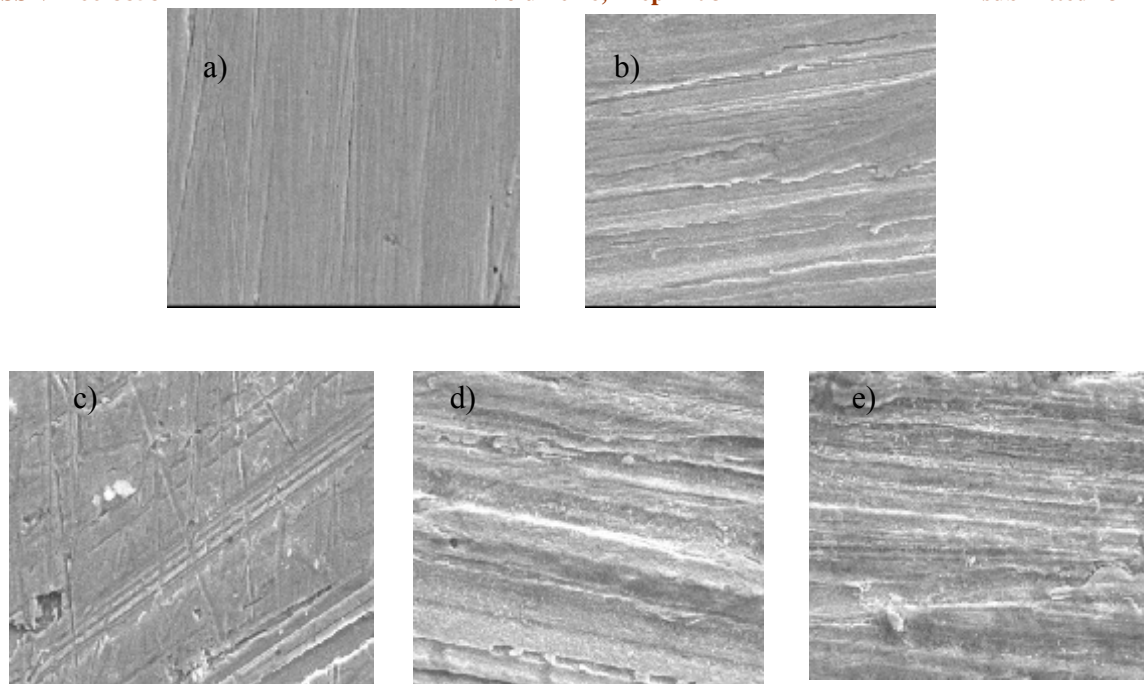
   d)   Rain water + PhPA (50 ppm) + Zn^{2+} (5 ppm)

Figure 4 SEM micrographs of Magnification-X 1000

- a) Carbon steel (control)
- b) Carbon steel immersed in rain water
- c) Carbon steel immersed in rain water containing ATMP (250 ppm) + Zn^{2+}(5 ppm)
- d) Carbon steel immersed in rain water containing DTPMP (50 ppm)+ Zn^{2+}(5 ppm)
- e) Carbon steel immersed in rain water containing PhPA (50 ppm)+ Zn^{2+}(5 ppm)
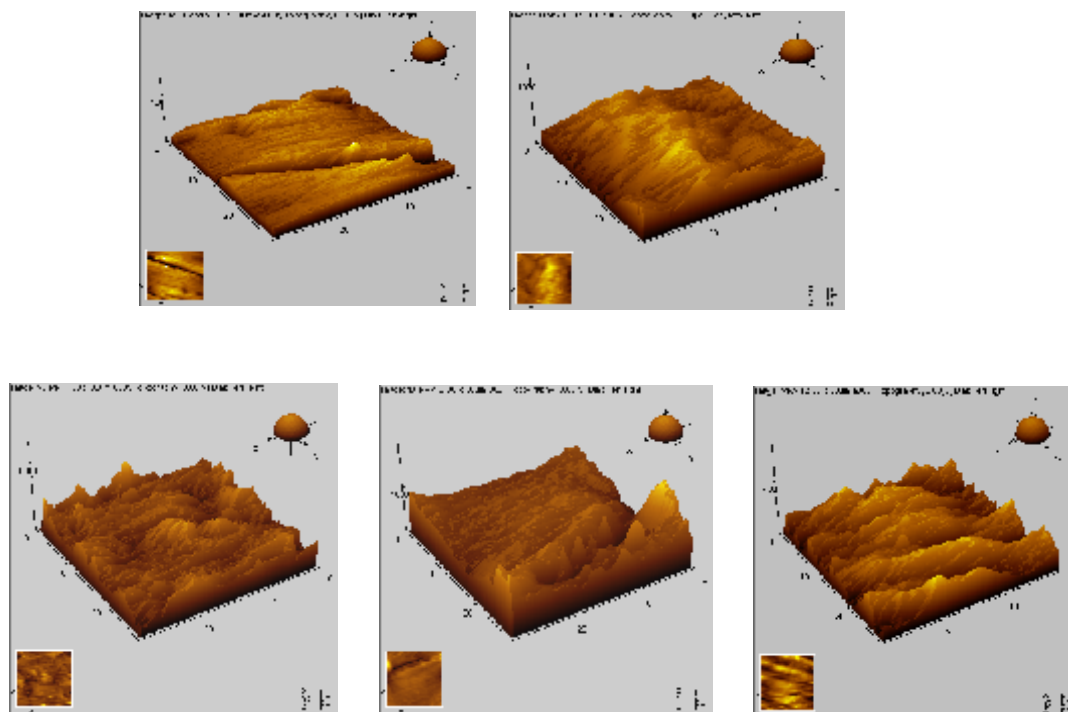
Figure 5   3D AFM images of the surface of

a)   Carbon steel (control)

b)   Carbon steel immersed in rain water

c)   Carbon steel immersed in rain water containing ATMP (250 ppm) + Zn^{2+}(5 ppm)

d)   Carbon steel immersed in rain water containing DTPMP (50 ppm)+ Zn^{2+}(5 ppm)

e)   Carbon steel immersed in rain water containing PhPA (50 ppm)+ Zn^{2+}(5 ppm)
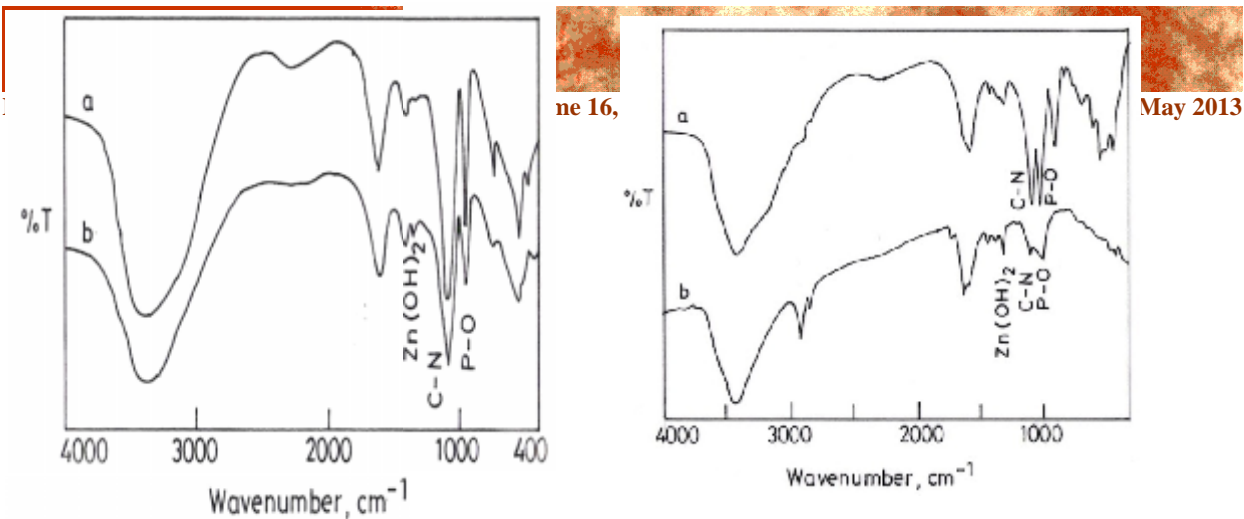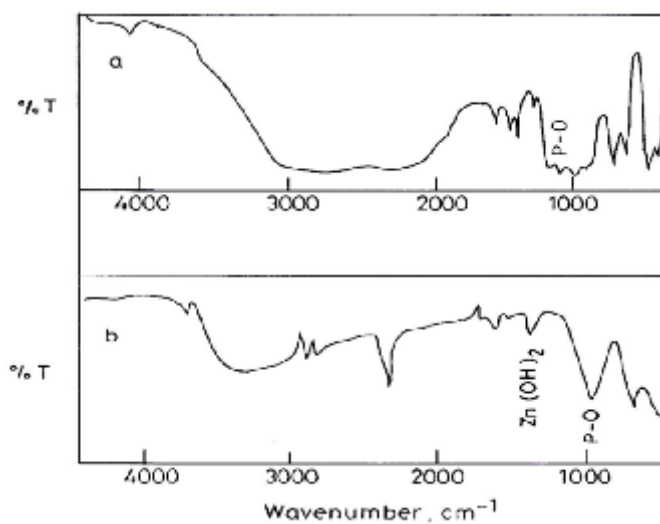
Fig 6 FTIR Spectra

a) Pure ATMP

b) Film formed on surface of metal after immersion in rainwater + ATMP (250 ppm) + Zn^{2+} (5 ppm)

a) Pure DTPMP

b) Film formed on surface of metal after immersion in rainwater + DTPMP (50 ppm) + Zn^{2+} (5 ppm).

a) Pure PhPA

b) Film formed on surface of metal after immersion in rainwater + PhPA (50 ppm) + Zn^{2+} (5 ppm).

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