



## Phosphonic Acids as Corrosion Inhibitor for Carbon Steel in Rainwater Collected from Rooftop-A Comparative Study

### KEYWORDS

carbon steel, phosphonic acids, corrosion inhibition, synergistic effect, electrochemical studies

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**ABSTRACT** 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<sup>2+</sup>. A synergistic effect exists between the phosphonic acids and Zn<sup>2+</sup>. The protective film formed on the metal surface was confirmed by FTIR spectroscopy, Atomic Force Microscopy and Scanning Electron Microscopy.

### Introduction

Phosphonates are molecules that contain one or more groups R-PO(OH)<sub>2</sub>. Their good chemical stability and solubility in water make possible their use in the inhibition of corrosion and scale formation<sup>1</sup>. 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<sup>2</sup>. 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<sup>3-5</sup>. The presence of Ca<sup>2+</sup> and Zn<sup>2+</sup> ions enhances the inhibition efficiency by synergism<sup>6-8</sup>. In the present study the inhibition effect of phosphonic acids such as amino(trimethylenephosphonic acid) (ATMP), diethylene triaminepenta(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<sup>2+</sup> 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 was measured by atomic force microscopy (AFM). The surface morphology of the carbon steel was shown by (scanning electron microscopy)SEM.

### Experimental

The inhibitory behaviors of amino(trimethylenephosphonic acid) (ATMP), diethylenetriaminepenta(methylenephosphonic acid) (DTPMP) and phenyl phosphonic acid (PhPA) were determined by weight loss method. The environment chosen is the rain water collected from roof top and stored in concrete tank. The pH was 8. The total dissolved salt and total hardness was found to be 55 ppm and 20 ppm respectively. 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. Weights of the specimens before and after immersion were determined using a balance, Shimadzu AY62 model. The corrosion rates were then calculated. The electrochemical studies such as potentiostatic polarization study and AC impedance measurements were 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<sup>2</sup> area exposed. A saturated calomel electrode (SCE) was used as reference electrode. A rectangular platinum foil was used as the counter electrodes. The nature of the film formed on the surface of the metal specimens was analyzed by various surface analysis techniques. The surface morphology measurements of the carbon steel were examined using Hitachi S-3000 H computer controlled scanning electron microscope (SEM) and atomic force microscopy (AFM) using PicoSPM 2100 with the software version of Picoscan version 5. The FTIR spectra of the protective film formed on the metal surface were recorded using Perkin - Elmer 1600 FTIR spectrophotometer with a resolving power of 4 cm<sup>-1</sup>.

### Inhibitors and Solutions

The molecular structure of inhibitors used is shown in the Figure 1.

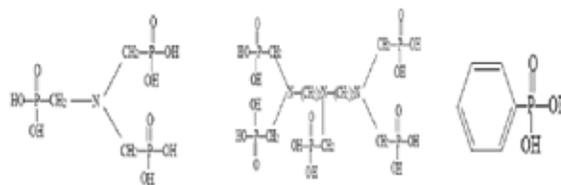


Figure1. ATMP DTPMP PhPA

All the inhibitor solutions are prepared by neutralising and made with distilled water.

### Results and Discussion

The percentage inhibition efficiency of the various inhibi-

tor 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 4.

The corrosion inhibition efficiency of the phosphonic acids used is in the order of ATMP > DTPMP > PhPA. The interactions of inhibitors with metal surfaces have been discussed in relation to Pearson's 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 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 disfavours adsorption of additional phosphonate molecules<sup>10</sup>. 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<sup>11</sup>. 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<sup>2+</sup>. PhPA shows less IE due to the bulk precipitation of a Zn<sup>2+</sup>-PhPA complex will lead to a loss of active inhibitor to precipitation, leading to insufficient levels to adhere on to the metal surface and to form protective film<sup>12</sup>. Further the IE of phosphonic acids has enhanced in the presence of ZnSO<sub>4</sub>. This is supported by the fact that synergism parameter, S<sub>p</sub> > unity<sup>13-15</sup> as shown in Table 1.

The corrosion parameters of carbon steel immersed in various test solutions obtained by polarization study are given in Table 2. It is observed from Table 2 that the corrosion potential for all the inhibitor system shifts to the anodic (noble) direction when compared with that of E<sub>corr</sub> 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 are transported to the anodic sites in the presence of Zn<sup>2+</sup>. 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 phosphonic acids - Fe<sup>2+</sup> surface layer. It was discussed in the literature<sup>16</sup> 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.

The AC impedance parameters, namely, charge transfer resistance (R<sub>c</sub>) and double layer capacitance (C<sub>dl</sub>) are given in Table 2. It is inferred that the charge transfer resistance (R<sub>c</sub>) value of the inhibitor increases tremendously from that of the blank. Also, the double layer capacitance (C<sub>dl</sub>) decreases when compared with the C<sub>dl</sub> value of the blank. This suggests that a protective film is formed on the surface of the metal. The greater increase in the R<sub>c</sub> value, among the phosphonates is found for ATMP - Zn<sup>2+</sup> system. This accounts for the very high IE of ATMP - Zn<sup>2+</sup> system. Also the inhibition efficiencies derived from impedance data have been compared with those obtained

from polarization and weight loss measurements (table 4). 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.

### Surface Analysis of Metal Surface

SEM provides a pictorial representation of the surface. These images (Figure 2 c, d, e) suggest that in the presence of ATMP, DTPMP along with Zn<sup>2+</sup> inhibitor system the surfaces 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<sup>2+</sup>. Atomic force microscopy is a powerful technique for the gathering of roughness statistics from a variety of surfaces<sup>17</sup>. AFM is becoming an accepted method of roughness investigation<sup>18,19</sup>. Table 3 is summary of the average roughness (Ra), rms roughness (Rq) and maximum peak-to-valley height (P-V) value for carbon steel surface immersed in different environments. The significant reduction of these roughness parameters (value of Rq, Ra and P-V height) confirms that the surface appears smoother and also provides further evidence for the phosphonic acids inhibition efficiency order as ATMP > DTPMP > PhPA. The three dimensional (3D) AFM morphologies as shown in Figure 2. (c, d, e) display 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. 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 in Figure 3. 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<sup>2+</sup>-Phosphonic acid complex on the anodic sites of the metal surface<sup>20-22</sup>. The band at 1350 cm<sup>-1</sup> is due to Zn(OH)<sub>2</sub><sup>23-24</sup>.

### Conclusion

The results of the weight - loss study show that the phosphonic acids and Zn<sup>2+</sup> formulation controls corrosion of carbon steel in rain water. A synergistic effect exists between Zn<sup>2+</sup> 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<sup>2+</sup>-Phosphonic acid complex and Zn(OH)<sub>2</sub>.

When the solution containing rain water, phosphonic acids and Zn<sup>2+</sup> are prepared, there is formation of Zn<sup>2+</sup>-phosphonic acids complex in solution. When carbon steel is immersed in this solution, the Zn<sup>2+</sup>- phosphonic acids complex diffuses from the bulk of the solution towards metal surface. On the metal surface, Zn<sup>2+</sup>-phosphonic acids complex is converted into Fe<sup>2+</sup>- phosphonic acids complex on the anodic sites. Zn<sup>2+</sup> is released and combines with OH<sup>-</sup> to form Zn(OH)<sub>2</sub> on the cathodic sites.

**Table 1. Inhibition efficiencies for various concentrations of Phosphonic acids Zn<sup>2+</sup> 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 <sup>2+</sup> (5 ppm)	Inhibition efficiency (IE %)					
	0	50	100	150	200	250
ATMP	-10 (0.0994)	40 *(0.0510) **(1.65)	52 (0.0434) (1.72)	55 (0.0407) (1.76)	60 (0.0361) (1.93)	98 (0.0018) (35.75)
DTPMP	-10 (0.0994)	90 *(0.0090) **(10.1)	84 (0.0145) (5.02)	82 (0.0163) (3.79)	80 (0.0180) (3.03)	78 (0.0198) (2.5)
PhPA	-10 (0.0994)	85 *(0.0135) **(2.42)	70 (0.0271) (1.10)	60 (0.0361) (2.23)	46 (0.0487) (1.75)	34 (0.0596) (1.47)

\* Corrosion rate in mm/y \*\* Synergism parameter (S<sub>i</sub>)

**Table 2. 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**

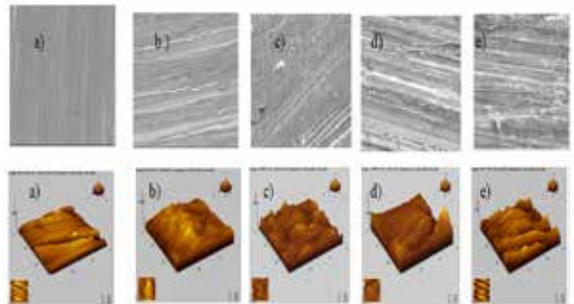
Inhibitor system	Polarization parameters				AC Impedance parameters	
	E <sub>corr</sub> mV vs SCE	b <sub>a</sub> mV/decade	b <sub>c</sub> mV/decade	I <sub>corr</sub> A/cm <sup>2</sup>	R <sub>t</sub> Ω cm <sup>2</sup>	C <sub>dl</sub> μF cm <sup>-2</sup>
Rain water	-710	270	215	3.981x 10 <sup>-5</sup>	931	441x 10 <sup>-6</sup>
Rain water + ATMP (250 ppm) + Zn <sup>2+</sup> (5 ppm)	-548	56	57	3.162x 10 <sup>-7</sup>	2229	237x 10 <sup>-6</sup>
Rain water + DTPMP (50 ppm) + Zn <sup>2+</sup> (5 ppm)	-540	103	103	6.723x 10 <sup>-6</sup>	2306	370x 10 <sup>-6</sup>
Rain water + PhPA (50 ppm) + Zn <sup>2+</sup> (5 ppm)	-540	55	57	3.359x 10 <sup>-6</sup>	1589	333x 10 <sup>-6</sup>

**Table 3. The average roughness (Ra), RMS roughness (Rq), maximum peak-to-valley height (P-V) value for carbon steel surface immersed in different environments**

Samples	RMS Roughness (Rq) (nm)	Average Roughness (Ra) (nm)	Maximum peak-to-valley height (P-V) (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 <sup>2+</sup> (5 ppm)	396	323	2402.76
Carbon steel immersed in rain water containing DTPMP (50 ppm) and Zn <sup>2+</sup> (5 ppm)	537	465	2353
Carbon steel immersed in rain water containing PhPA (50 ppm) and Zn <sup>2+</sup> (5 ppm)	708	590	3100

**Table 4. Comparison of percentage inhibition efficiencies obtained from different methods**

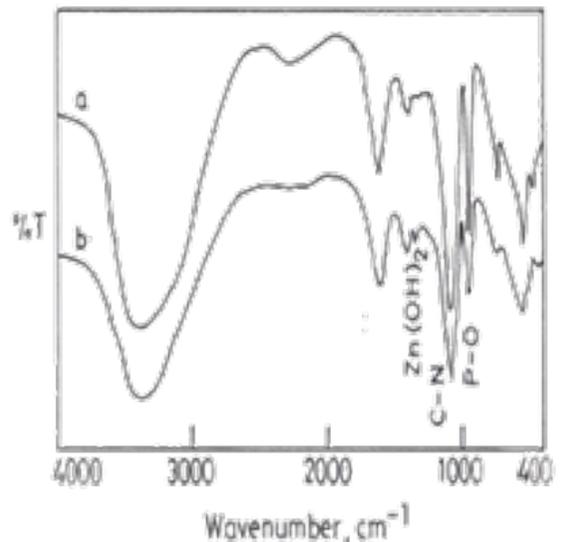
Inhibitors system	Inhibition efficiency (IE %)		
	Using weight loss method	Using Polarization Technique	Using Impedance technique
Rain water + ATMP (250 ppm) + Zn <sup>2+</sup> (5 ppm)	98	99	58
Rain water + DTPMP (50 ppm) + Zn <sup>2+</sup> (5 ppm)	90	83	60
Rain water + PhPA (50 ppm) + Zn <sup>2+</sup>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



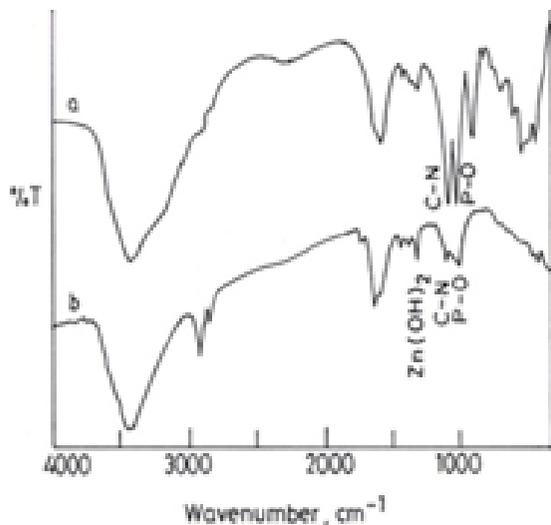
**Figure 2. SEM micrographs and 3D AFM images of the surface of**

- a) Carbon steel (control)
- b) Carbon steel immersed in rain water
- c) Carbon steel immersed in rain water containing ATMP (250 ppm) + Zn<sup>2+</sup> (5 ppm)
- d) Carbon steel immersed in rain water containing DTPMP (50 ppm) + Zn<sup>2+</sup> (5 ppm)
- e) Carbon steel immersed in rain water containing PhPA (50 ppm) + Zn<sup>2+</sup> (5 ppm)

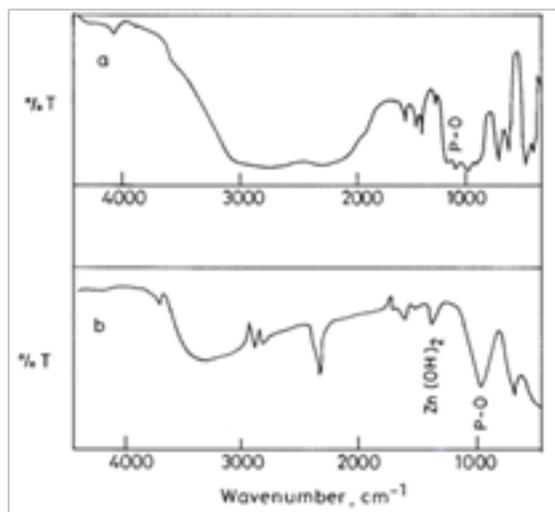
**Figure 3. FTIR Spectra**



- a) Pure ATMP
- b) Film formed on surface of metal immersed in ATMP and Zn<sup>2+</sup>



a) Pure DTPMP  
b) Film formed on surface of metal immersed in DTPMP and Zn<sup>2+</sup>



a) Pure PhPA  
b) Film formed on surface of metal immersed in PhPA + Zn<sup>2+</sup>

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