



## INHIBITIVE BEHAVIOUR OF GREEN INHIBITOR IN POTABLE WATER DISTRIBUTION SYSTEM

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### ABSTRACT

The inhibition effect of amino trimethylene phosphonic acid (ATMP) and zinc ions on the corrosion of carbon steel in potable water distribution system was investigated. The corrosion inhibiting action was studied through weight loss, potentiodynamic polarization and AC impedance spectroscopy techniques. The possibilities of formation of protective complex was examined using UV – visible spectroscopy. The investigations revealed that zinc acts as an excellent synergist in corrosion inhibition. UV – visible spectral study indicates that there will be a possibility of formation of complexes of ATMP and  $Zn^{2+}$  with carbon steel iron. Polarization studies indicate that the new binary system is a mixed inhibitor. Result of the impedance studies shows that a protective film is formed on the metal surface in presence of the inhibitor formulation.

### Indexing terms/Keywords

Phosphonic acid; weight loss; synergism; spectral and electrochemical studies

### Academic Discipline And Sub-Disciplines

Chemistry/Electrochemistry

### SUBJECT CLASSIFICATION

Corrosion

### TYPE (METHOD/APPROACH)

Experimental study

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## 1. INTRODUCTION

From economic point of view, obstruction to flow is the major problem due to corrosion products in a potable water distribution system. Increased pumping costs of \$40 million a year have been estimated to result from obstruction of flow by corrosion products [1]. Corrosion of water heaters poses a much more expensive problem. Replacement costs have been estimated at \$300 million a year [1]. Potable waters vary quite widely in composition. Dissolved solids range from about 20 mg/l to over 2 g/l. Over 100 public supplies exceeded 2 g/l total solids in 1962 [2]. Dissolved oxygen does not render pure water particularly corrosive, at least at normal temperatures. However, additions of traces of sulphate or chloride (i.e., 0.55 mg/l) suffice to make it highly aggressive [3]. Larson and co-workers [4-6] have found that chlorides, sulphates and nitrates stimulate corrosion of iron in oxygen bearing water, while calcium, bicarbonate and hydroxide were inhibitive.

The use of zinc salts with the polyphosphates markedly accelerates the establishment of protection [7-9]. Zinc repair also is accelerated by zinc which may be incorporated in the phosphate glass or may be fed separately as a soluble salt. Optimum zinc and polyphosphate dosages are somewhat interdependent. Higher zinc levels and vice versa. However, zinc dosages generally are fixed at a definite percentage (i.e., between 9 and 10%) of the polyphosphate feed. Thus, the normal operating level of zinc is well below the allowable limit (5 mg/l or 5ppm) for a potable supply [2]. Since the polyphosphate in the reason for microbial corrosion and conversion into orthophosphate, an alternate is needed. Though many inhibitors are available the selective is limited by considering the portability.

The present work was designed to study the corrosion inhibition of carbon steel in potable water by ATMP and zinc ions as corrosion inhibitors using three different techniques: weight loss, electrochemical studies and UV – visible spectroscopy techniques, hoping to get some general ideas to guide the composing of inhibitor in reality.

## 2. EXPERIMENTAL DETAILS

### 2.1 Materials

The composition of carbon steel used for corrosion inhibition studies was (Wt %): 0.026% S, 0.06% P, 0.4% Mn, 0.1% C and balance being Fe. The specimens of size 1.0cm×4.0cm×0.2cm were press cut from the carbon steel sheet, were machined and abraded with a series of emery papers.

This was followed by rinsing in acetone and bidistilled water and finally dried in air. Before any experiment, the substrates were treated as described and freshly used with no further storage. The inhibitors ATMP, molecular mass 573.20g mol<sup>-1</sup>, Zn<sup>2+</sup> ions were used as received. A stock solution of 1000ppm of ATMP was prepared in bidistilled water and the desired concentration was obtained by appropriate dilution. The concentration of ATMP used for the study ranges from 10 to 150ppm. All solutions were prepared using potable water (Tiruchirappalli, Tamil Nadu, India). The study was carried out at room temperature. The molecular structure of ATMP is given in Fig 1.

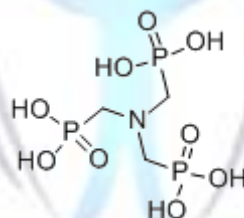


Figure 1. Molecular structure of ATMP

### 2.2 Weight - loss Measurements

The freshly prepared carbon steel specimens were suspended in 150ml beakers containing 100ml of test solution maintained at room temperature with the aid of glass rods and hooks. The weight loss taken was the difference between the weight at a given time and the original weight of the specimens. The measurements were carried out for the uninhibited solution and the solution containing ATMP and ATMP - Zn<sup>2+</sup> mixture. Weight loss experiments were performed for the duration of seven days. The specimens were immersed in triplicate and the average corrosion rate was calculated. These uncertainties or RSD for three replicate measurements were less than 5%. The corrosion rates (C<sub>R</sub>) were determined using the equation:

$$CR \left( \frac{mm}{y} \right) = \frac{87.6 \times w}{a t D}$$

where w = corrosion weight loss of carbon steel (mg)

a = area of the coupon (cm<sup>2</sup>)

t = exposure time (h)

D = density of the carbon steel (g cm<sup>-3</sup>).



The inhibition efficiency (IE) of ATMP -  $Zn^{2+}$  mixture was calculated by using the following equation:

$$\%IE = \frac{C_{Ro} - C_{Ri}}{C_{Ro}} \times 100$$

where  $C_{Ro}$  = corrosion rate of carbon steel in the absence of inhibitor

$C_{Ri}$  = corrosion rate of carbon steel in the presence of inhibitor

## 2.2. Electrochemical studies

Both the potentiodynamic polarization studies and electrochemical impedance spectroscopic (EIS) studies were carried out using the electrochemical workstation model CHI- 760d and the experimental data were analysed by using the electrochemical software (Version: 12.22.0.0). The measurements were conducted in a conventional three electrode cylindrical glass cell with platinum electrode as auxiliary electrode and saturated calomel electrode as reference electrode. The working electrode was carbon steel embedded in epoxy resin of polytetrafluoroethylene so that the flat surface of  $1\text{cm}^2$  was the only surface exposed to the electrolyte.

The three electrodes set up was immersed in control solution of volume 100ml both in the absence and presence of the inhibitors formulations and allowed to attain a stable open circuit potential (OCP). The pH values of the solution were adjusted to 7.0 and the solutions were unstirred during the experiments. Polarization curves were recorded in the potential range of -750 to -150 mV with a resolution of 2mV. The curves were recorded in the dynamic scan mode with a scan rate of  $2\text{mVS}^{-1}$  in the current range of -20mA to +20mA. The Ohmic drop compensation has been made during the studies. The corrosion potential ( $E_{corr}$ ), corrosion current ( $I_{corr}$ ), anodic Tafel slope ( $\beta_a$ ) and cathodic Tafel slope ( $\beta_c$ ) were obtained by extrapolation of anodic and cathodic regions of the Tafel plots.

Electrochemical impedance spectra in the form of Nyquist plots were recorded at OCP in the frequency range from 60KHz to 10MHz with 4 to 10 steps per decade. A sine wave, with 10mV amplitude, was used to perturb the system. The impedance parameters viz., charge transfer resistance ( $R_{ct}$ ), double layer capacitance ( $C_{dl}$ ) were obtained from the Nyquist plots.

## 2.3. The UV- Visible absorption spectra

The possibility of formation of  $Zn^{2+}$  - phosphonic acid complex in solutions was examined by mixing the respective solutions and recording their UV –visible absorption spectra using Hitachi U -3400 spectrophotometer.

## 3. RESULTS AND DISCUSSION

### 3.1 Weight-loss measurements

The inhibition actions of ATMP and  $Zn^{2+}$  in controlling corrosion of carbon steel immersed in potable water for a duration of seven days in the both without and with of ATMP and  $Zn^{2+}$  is given in Table 1. It can be seen from data that  $Zn^{2+}$  alone has some IE and ATMP alone is poor inhibitor and is found to be corrosive. For example 150ppm of ATMP has 27% IE and 5ppm of  $Zn^{2+}$  has 8% IE. However the combination of 150ppm of ATMP and 5ppm of  $Zn^{2+}$  has 78% IE. This is found to be the maximum IE obtained by the system. This clearly suggests that ATMP and  $Zn^{2+}$  mutually enhance the inhibition efficiency of each other in controlling the corrosion of carbon steel.

The synergism is due to the formation of complex with ATMP and the role of  $Zn^{2+}$  is to transport the ATMP inhibitor from the bulk of the solution onto the metal surface [10-12].



**Table 1. Corrosion Inhibition efficiency of carbon steel in potable water system, with and without addition of inhibitor obtained by the weight loss method.**

Concentration of Zn <sup>2+</sup> (ppm)	Concentration of ATMP (ppm)	Corrosion Rate (C <sub>R</sub> ) mmy <sup>-1</sup>	Inhibition efficiency (%)	Surface coverage (θ)
-	-	311.1	-	-
-	-	283.9	8	0.08
-	10	361.7	-16	0.16
-	25	330.6	-6	0.06
-	50	299.4	3	0.03
-	75	280.0	10	0.10
-	100	266.4	14	0.14
-	125	245.0	21	0.21
-	150	225.5	27	0.27
5	10	280.0	10	0.10
5	25	233.3	25	0.25
5	50	194.4	37	0.37
5	75	157.5	49	0.49
5	100	134.1	57	0.57
5	125	105.0	66	0.66
5	150	66.1	78	0.78

### 3.2 Influence of duration of immersion on the inhibition efficiency of Zn<sup>2+</sup> and ATMP system.

When 5ppm Zn<sup>2+</sup> is added to the various ATMP concentrated solution, there is a increase in I.E in particular day but when Time Period increases I.E also decreases due to desorption of protective complex into bulk.

**Table 2. Influence of immersion period on the IE and corrosion rate of ATMP –Zn<sup>2+</sup> (5ppm) system**

Duration		1		3		5		7	
Con. Of Zn <sup>2+</sup> (ppm)	Con. Of ATMP (ppm)	C <sub>R</sub> mmy <sup>-1</sup>	IE (%)	C <sub>R</sub> mmy <sup>-1</sup>	IE (%)	C <sub>R</sub> mmy <sup>-1</sup>	IE (%)	C <sub>R</sub> mmy <sup>-1</sup>	IE (%)
-	-	5.8	-	70.0	-	138.9	-	311.1	-
5	10	5.0	14	60.0	14	104.1	25	280.0	10
5	25	4.4	23	56.6	19	93.0	33	233.3	25
5	50	3.8	33	50.0	28	76.4	45	194.4	37
5	75	3.3	42	45.0	36	70.8	49	157.5	49
5	100	2.5	57	29.1	58	59.7	57	134.1	57
5	125	1.6	71	17.5	75	43.0	69	105.0	66
5	150	0.5	90	10.8	84	27.7	80	66.1	78

### 3.3 Potentiodynamic Polarization study

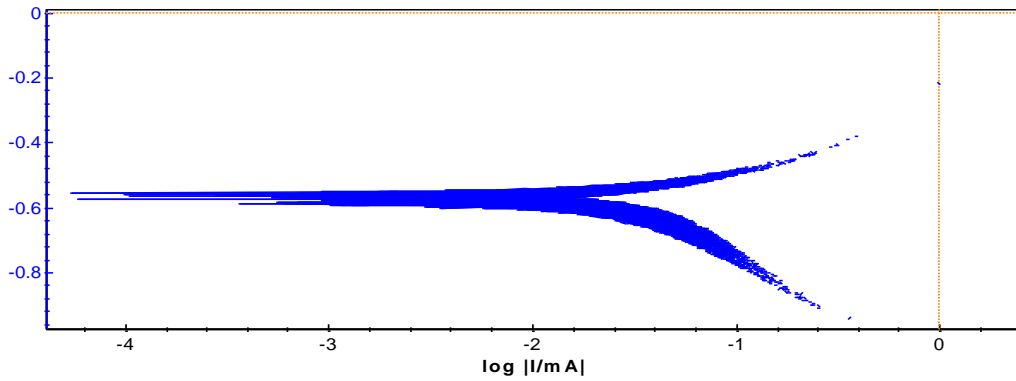


Figure 2a. Without inhibitor

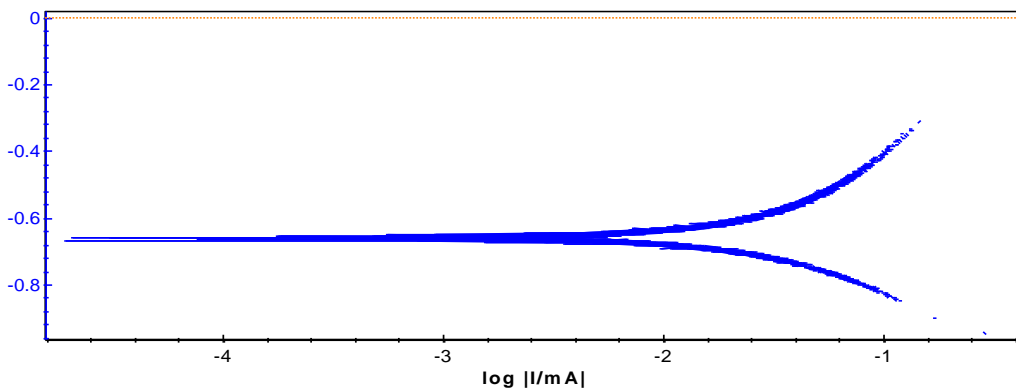


Figure 2b. With inhibitor (5ppm Zn<sup>2+</sup> + 150 ppm ATMP)

Show polarization curve of carbon steel in potable water without and with of inhibitor. It was found that the values of corrosion current density ( $I_{corr}$ ) of carbon steel in the potable water with inhibitor were smaller than without addition of inhibitor.

Furthermore, as presented in Fig. 2b. the addition of 5ppm Zn<sup>2+</sup> + 150ppm ATMP shifts the corrosion potential ( $E_{corr}$ ) value (-625.045mV to -646.094mV) in presence inhibitor according to Ferreira and W.H. Li if the displacement in corrosion potential is more than 85mV with respect to the corrosion potential of the blank, the inhibitor can be seen as cathodic or anodic type [13-14]. The maximum displacement was < 21mV which indicated that the studied inhibitor and the effect is more evident at higher concentrations. These results suggest that the studied formulation can be classified as mixed type inhibitor.

Table 3. Tafel parameters for carbon steel in potable water system in without and with addition of inhibitors

S.No	Conc. Of Zn <sup>2+</sup> (ppm)	Conc. Of ATMP (ppm)	$E_{corr}$ mV	$I_{corr}$ mV	$\beta_a$ mV	$\beta_c$ mV
1	Blank	-	-625.04	31.79	228.6	221.3
2	5	150	-646.09	19.95	296.7	258.9

### 3.4 AC Impedance Spectra

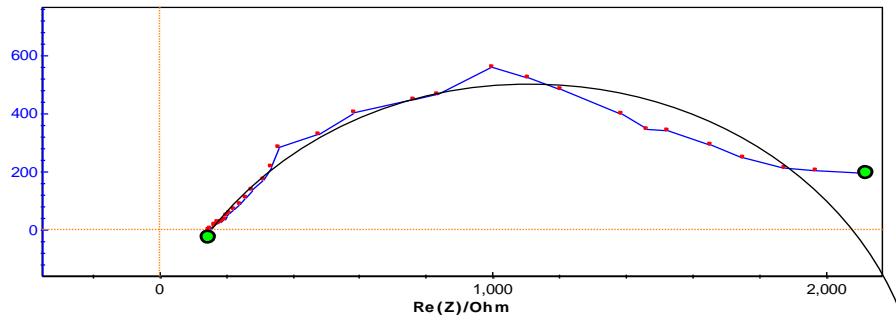


Figure 3a. Without inhibitor

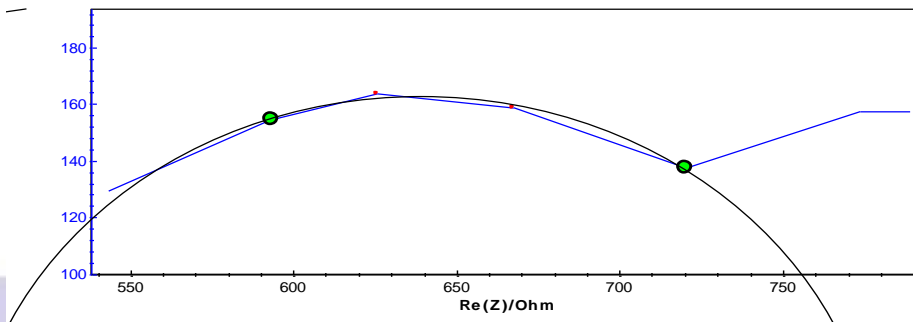


Figure 3b. With inhibitor (5ppm Zn<sup>2+</sup> + 150 ppm ATMP)

The Nyquist plots of carbon steel immersed in potable water is shown in Fig. 3a. and Fig. 3b. The Nyquist parameters namely, charge transfer resistance ( $R_{ct}$ ) and double layer capacitance ( $C_{dl}$ ) are given in Table 4. Without inhibitor system, the low  $R_{ct}$  value and higher  $C_{dl}$  value and with inhibitor system, the high  $R_{ct}$  value and lower  $C_{dl}$ . These values confirm that the formation of a protective film onto the metal surface.

Table 4. Nyquist parameters for carbon steel in potable water system in without and with addition of inhibitors.

S.No	Conc. of Zn <sup>2+</sup> (ppm)	Conc. of ATMP (ppm)	$R_{ct}$ (ohm)	$C_{dl}$ F.cm <sup>-2</sup> × 10 <sup>-6</sup>
1	Blank	-	276.5	16.05
2	5	150	1919	1.23

### 3.5 Analyses of UV-visible spectra

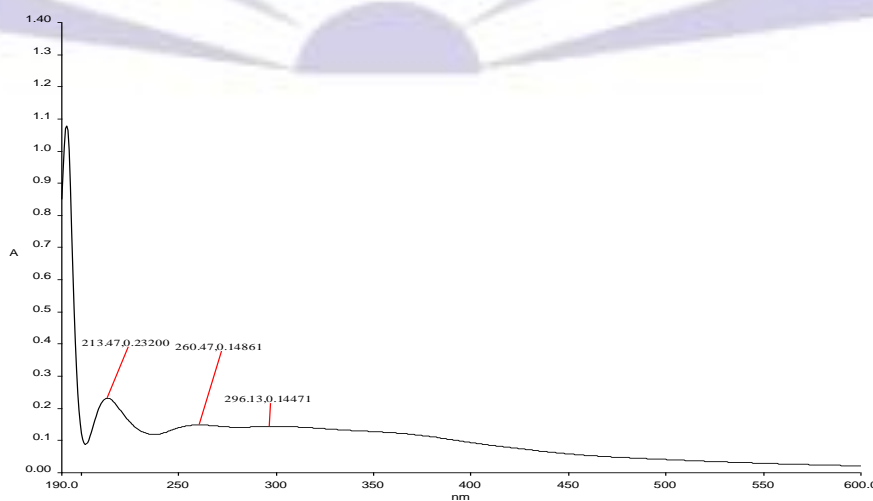
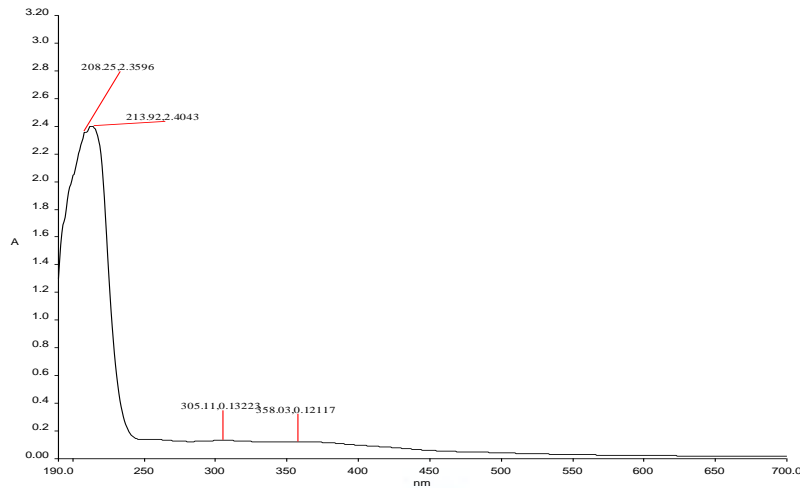


Figure 4. Without Inhibitor



**Figure 4a. With inhibitor (5ppm Zn<sup>2+</sup> + 150ppm ATMP + 100ppm Fe<sup>2+</sup>)**

UV- visible absorption spectra can be used to confirm the possibility of formation protective film on the metal surface [15-16]. UV- visible absorption spectrum of ATMP and Zn<sup>2+</sup> is shown in Fig.4. A remarkable increase in absorbance is noticed in Fig. 4a than in Fig. 4b. These observations indicate that there is a formation of Zn<sup>2+</sup> - ATMP complex and Fe<sup>2+</sup> - ATMP complex in solution.

#### 4. CONCLUSION

The following main conclusions are drawn from the present study:

- The binary formulation (5 ppm Zn<sup>2+</sup> and 150ppm ATMP) has good inhibition effect for the corrosion of carbon steel in potable water system.
- Significant synergism was attained by the combined application of 5ppm Zn<sup>2+</sup> -150ppm ATMP system
- Polarization data showed that the investigated inhibition formulation acts as a mixed type inhibitor.
- AC impedance spectra reveal that a protective film is formed onto carbon steel surface
- UV-visible spectral study indicates that there was a possibility of formation of complexes.
- This new inhibitor formulation is more eco- friendly.

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