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# Gravimetric Studies Of A New Ternary Corrosion Inhibitor Formulation For Carbon Steel In Industrial Cooling Water Systems

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## Abstract

*Results of gravimetric studies of corrosion control of carbon steel using Nitrilotris(methylene-phosphonic acid) (NTMP) and $Zn^{2+}$ in combination with nicotinic acid as a synergist, are discussed. The present study infers that nicotinic acid acts as an excellent synergist in corrosion inhibition. The new ternary formulation is effective at relatively low concentrations of both NTMP and $Zn^{2+}$. Optimum concentrations of NTMP and $Zn^{2+}$ in combination with nicotinic acid for an effective inhibition are 30 ppm and 20 ppm respectively. The formulation is effective in the pH range 5 to 9. Minimum dosages of NTMP, $Zn^{2+}$ and nicotinic acid for maintenance of the protective film are 10, 15 and 40 ppm respectively. Moreover, the inhibiting action of the film is retained for longer immersion periods upon providing these maintenance dosages. Thus, the ternary formulation is more environmentally friendly. The formulation shows good inhibition even in hydrodynamic conditions, inferring the possibility of its practical applications in industrial cooling water systems.*

## 1. Introduction

Carbon steel is the main construction material for industrial cooling water systems. Corrosion of carbon steel is one of the major challenges in such systems. Phosphonate based formulations are well-known for their ability to inhibit corrosion of carbon steel in low chloride aqueous environment [1-3]. However, the major drawback of such formulations is the requirement of higher concentrations of both phosphonate and $Zn^{2+}$ to achieve good inhibition. But, the disposal of higher levels of $Zn^{2+}$ in wastewaters from industries is objectionable according to environmental guidelines. In order to overcome this limitation in applying phosphonate based inhibitor formulations, a third component, generally a non-toxic compound, is added to phosphonate-$Zn^{2+}$ systems. The resulting ternary formulations are effective at relatively low concentrations of both phosphonate and $Zn^{2+}$ [4-6].

In this background, a commercially important phosphonic acid namely nitrilotris(methylene-phosphonic acid) (NTMP) has been chosen in the present study. NTMP contains three phosphonic acid groups which can participate in complex formation with metal ions like $Zn^{2+}$. The organic additive chosen as synergist to NTMP-$Zn^{2+}$ binary system is nicotinic acid. Nicotinic acid (Vitamin $B_3$) is a simple molecule consisting of one nitrogen atom in aromatic ring and one carboxylic acid group. In the present study, optimum concentrations of all the three components namely NTMP, $Zn^{2+}$ and nicotinic acid to achieve good inhibition efficiency, were determined. The effects of pH and hydrodynamic conditions on inhibition efficiency of the ternary formulation were also determined. Dosages of inhibitor components required for maintenance of the protective film and effect of longer immersion periods on inhibition efficiency were also evaluated.



## 2. Methods and Materials

All the results included in the present study are entirely based on gravimetric measurements. These measurements provide information on the amount of material loss by corrosion over a specified period of time and under specified operating conditions [7]. However, they require a long time for corrosion rate determinations. For all the studies, the specimens taken from a single sheet of carbon steel of the following composition were chosen. C – 0.1 to 0.2 %, P – 0.04 to 0.07 %, S – 0.03 to 0.04 %, Mn – 0.3 to 0.5 % and the rest iron. Prior to the tests, the specimens were polished to mirror finish with 1/0, 2/0, 3/0 and 4/0 emery polishing papers respectively, washed with distilled water, degreased with acetone and dried. The polished specimens of the dimensions, 3.5 cm x 1.5 cm x 0.2 cm, were used throughout the study. NTMP ($C_3H_{12}NO_9P_3$), Zinc sulphate ($ZnSO_4.7H_2O$), nicotinic acid ($C_6NH_5O_2$) and other reagents were analytical grade chemicals. Molecular structures of NTMP and nicotinic acid are shown in Figure 1. All the solutions were prepared with triple distilled water. The pH values of the solutions were adjusted by using 0.01 N NaOH and 0.01 N $H_2SO_4$ solutions. An aqueous solution consisting of 200 ppm of NaCl has been used as the control throughout the study because of the following reason. The water used in cooling water systems is generally either demineralised water or unpolluted surface water. In either case the aggressiveness of the water will never exceed that of 200 ppm of NaCl.

The polished specimens were weighed and immersed in duplicate, in 100 mL control solution in the absence and presence of inhibitor formulations of different concentrations, for a period of seven days. Then the specimens were reweighed after washing, degreasing and drying. During the studies, only those results were taken into consideration, in which the difference in the weight-loss of the two specimens immersed in the same solution did not exceed 0.1 mg. Accuracy in weighing up to 0.01 mg and in surface area measured up to 0.1 $cm^2$, as recommended by ASTM G31, was followed [8]. The immersion period of seven days was fixed in view of the considerable magnitude of the corrosion rate obtained in the absence of any inhibitor after this immersion period. The immersion period was maintained accurately up to 0.1 h in view of the lengthy immersion time of 168 h. Under these conditions of accuracy, the relative standard error in corrosion rate determinations is of the order of 2 % or less for an immersion time of 168 h [9].

Corrosion rates of carbon steel in the absence and presence of various inhibitor formulations were determined in mmpy. Inhibition efficiencies (IE) of the inhibitor formulations were calculated by using the formula,

$IE\ (\%) = 100\ [(CR)_o - (CR)_I] / (CR)_o$

where $(CR)_o$ and $(CR)_I$ are the corrosion rates in the absence and presence of inhibitor respectively.

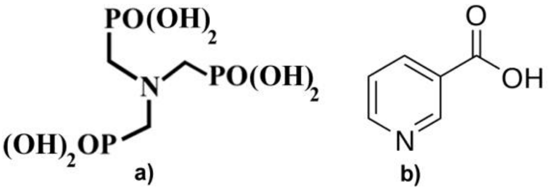


**Figure 1. Molecular structures of a) NTMP and b) Nicotinic acid**

Gravimetric studies were carried out using binary inhibitor formulation, NTMP-$Zn^{2+}$, in order to determine the required minimum concentrations of both NTMP and $Zn^{2+}$ for an effective inhibition at pH = 7. Based on these concentrations, NTMP and $Zn^{2+}$ were considered in the range of 20-40 ppm and 10-20 ppm respectively, in combination with 25-200 ppm of nicotinic acid. The influence of pH on inhibition efficiency of the effective ternary inhibitor formulation was also studied in the pH range, 4-10. Gravimetric experiments were also conducted using the specimens covered by the protective film in the ternary inhibitor formulation, in order to determine the required minimum dosage of each of the components for maintenance of the protective film in the chosen corrosive environment. Carbon steel specimens covered by protective films were immersed in aqueous solutions containing 200 ppm of NaCl and all the inhibitor components with required minimum dosages at pH = 7 for longer immersion periods up to 63 days. Based on the results, the effectiveness of the inhibitor formulation for longer immersion times is assessed. It was of interest of the authors to observe the suitability of the inhibitor under hydrodynamic conditions. The inhibitor formulation was tested under hydrodynamic conditions in view of the fact that the inhibitor formulations are expected to work practically under such conditions in recirculating cooling water systems. For these studies, single specimen was immersed in 200 ppm of NaCl in the absence as well as in presence of the inhibitor formulation and was kept for three days with different rotational speeds.

## 3. Results and discussion

### 3.1. Optimum concentrations of the inhibitor components

Results of gravimetric studies of corrosion inhibition of carbon steel using the binary inhibitor system, NTMP-$Zn^{2+}$, at pH = 7 are presented in Figure 2. From the figure, it can be inferred that the minimum concentrations of NTMP and $Zn^{2+}$ required for an effective inhibition are 50 ppm and 60 ppm respectively. With these compositions, the binary system afforded an inhibition efficiency (I.E.) of 97 %. It is expected that when the non-toxic organic additive namely nicotinic acid is added to the binary system, it can considerably reduce the concentrations of both NTMP and $Zn^{2+}$ required for an effective inhibition.

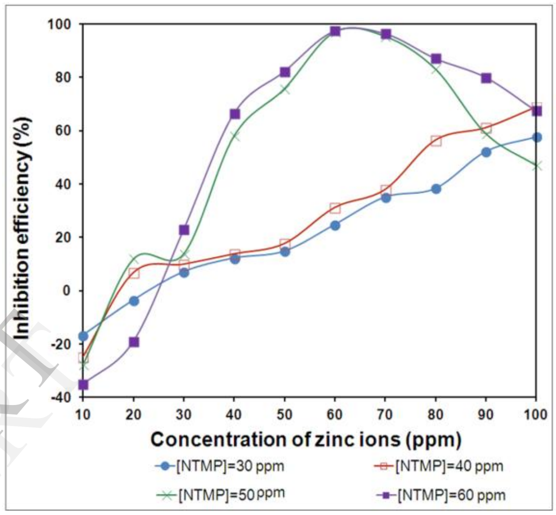


**Figure 2. Corrosion inhibition of carbon steel immersed in control solution containing NTMP (30-60 ppm) + $Zn^{2+}$, as a function of concentration of $Zn^{2+}$ at pH = 7**

Figure 3 shows the results of gravimetric studies of the ternary inhibitor system, NTMP (20-30 ppm) + $Zn^{2+}$ (15-20 ppm) + nicotinic acid (0-200 ppm) at pH = 7. It can be observed from the figure that when nicotinic acid is added to the combination of NTMP and $Zn^{2+}$ of any concentration, inhibition efficiency increases with increase in concentration of nicotinic acid, reaches a maximum value and then decreases. In other words, optimum concentrations of all the components are essential in order to exhibit a maximum value of inhibition efficiency. Ternary inhibitor formulation containing 10 ppm of $Zn^{2+}$ along with NTMP (20-40 ppm) and nicotinic acid (25-200 ppm) exhibited negligible values of inhibition efficiency. These results are not presented in the figure. From Figure 3, it can be concluded that minimum concentrations of NTMP, $Zn^{2+}$ and nicotinic acid required for exhibiting highest inhibition efficiency (I.E.) of 97.7 %, are 30 ppm, 20 ppm and 100 ppm respectively. At these concentrations of the components, the protected specimens are observed to be entirely covered by a multicoloured thin film. From this observation, it can be inferred that such film is protective and hence the observed highest inhibition efficiency. In literature, it was mentioned that phosphonate based inhibitor formulations are effective due to formation of protective surface films and that such films are composed of phosphonate-$Zn^{2+}$ complexes [1-3,10].

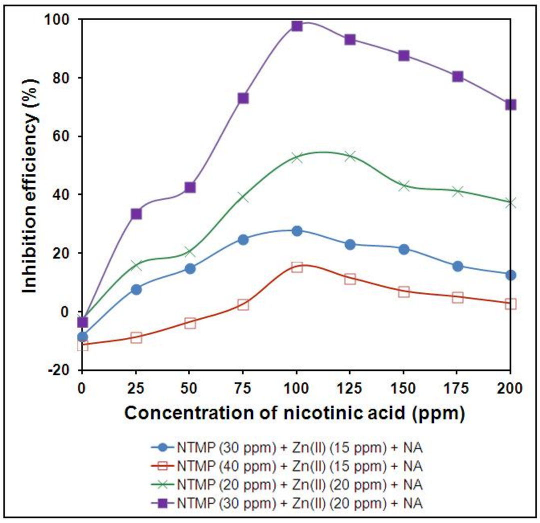


**Figure 3. Corrosion inhibition of carbon steel immersed in control solution containing NTMP (20-40 ppm) + $Zn^{2+}$ (15-20 ppm) + nicotinic acid, as a function of concentration of nicotinic acid at pH = 7**

### 3.2. Maintenance dosages and effect of immersion period

It can be expected that the concentrations of inhibitor components required for the maintenance of protective surface film are lower than those required for the formation of protective film. Hence, the inhibitor components with concentrations less than the optimum concentrations (corresponding to 97.7 % inhibition efficiency) are taken and the specimens already covered by the protective film are immersed for seven more days. The results of gravimetric studies are presented in Table 1. From the table, it can be inferred that the minimum concentrations of NTMP, $Zn^{2+}$ and nicotinic acid required for the maintenance of the highest inhibition efficiency are 10, 15 and 40 ppm respectively. These results indicate that only 15 ppm of $Zn^{2+}$ is sufficient to maintain the protective nature of the surface film. Hence, the ternary formulation is more environmentally friendly than NTMP-$Zn^{2+}$ binary system. Further, the immersion period of the specimens in the solutions containing maintenance dosage was extended from 7 days to 63 days and inhibition efficiency was determined at the intervals of 7 days. The results are presented in Table 2. From the table, it is interesting to note that the inhibition efficiency values of the inhibitor formulation with maintenance dosage are above 95 % at any immersion period up to 63 days considered in the present study. These results suggest that the protective film is maintained by the maintenance dosage for longer immersion times even up to 63 days.

**Table 1. Results of gravimetric measurements for maintenance dosages of the inhibitor components**

| Maintenance dosages of the inhibitor components (ppm) | | | Corrosion rate (mmpy) | I.E. (%) |
|---|---|---|---|---|
| NTMP | $Zn^{2+}$ | Nicotinic acid | | |
| 0 | 0 | 0 | 0.070608 | --- |
| 30 | 20 | 100 | 0.001594 | 97.74 |
| 30 | 15 | 100 | 0.001594 | 97.74 |
| 30 | 10 | 100 | 0.010021 | 85.80 |
| 30 | 5 | 100 | 0.020271 | 71.29 |
| 20 | 15 | 100 | 0.001822 | 97.42 |
| 10 | 15 | 100 | 0.002505 | 96.45 |
| 10 | 15 | 80 | 0.002505 | 96.45 |
| 10 | 15 | 60 | 0.002733 | 96.13 |
| 10 | 15 | 40 | 0.002961 | 95.80 |
| 10 | 15 | 20 | 0.014577 | 79.35 |



**Table 2. Effect of immersion period on corrosion inhibiting action of the ternary inhibitor formulation**

| Immersion period (days) | Control | Inhibitor | |
|---|---|---|---|
| | Corrosion rate (mmpy) | Corrosion rate (mmpy) | I.E. (%) |
| 7 | 0.070608 | 0.002961 | 95.80 |
| 14 | 0.070722 | 0.001708 | 97.58 |
| 21 | 0.071974 | 0.001138 | 98.41 |
| 28 | 0.073110 | 0.000911 | 98.75 |
| 35 | 0.073250 | 0.000774 | 98.94 |
| 42 | 0.075277 | 0.000645 | 99.14 |
| 49 | 0.075261 | 0.000715 | 99.05 |
| 56 | 0.079035 | 0.000740 | 99.06 |
| 63 | 0.081920 | 0.000683 | 99.16 |

### 3.3. Effects of pH and hydrodynamic conditions

Figure 4 shows the results of gravimetric studies of the effective inhibitor formulation at different pH values from 4 to 10. It indicates that the new ternary formulation is effective in the pH range 5 to 9. From pH 7 to 9, 100 ppm of nicotinic acid is required in combination with NTMP (30 ppm) + $Zn^{2+}$ (20 ppm) to achieve an inhibition efficiency > 97 %, while such an inhibition could be obtained with only 75 ppm of nicotinic acid in combination with NTMP (30 ppm) + $Zn^{2+}$ (20 ppm) at pH 5 and 6. The pH range of water used in recirculating cooling water systems will not exceed 5-9. Hence, this inhibitor formulation is well suited for such systems as far as pH is concerned.

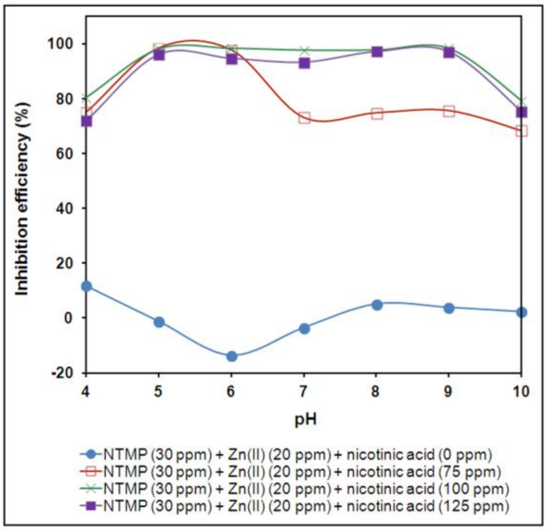


**Figure 4. Corrosion inhibition of carbon steel immersed in control solution containing NTMP (30 ppm) + $Zn^{2+}$ (20 ppm) + nicotinic acid, as a function of pH**

The results of studies on effect of hydrodynamic conditions on inhibition efficiency of the ternary inhibitor formulation, NTMP (30 ppm) + $Zn^{2+}$ (20 ppm) + nicotinic acid (100 ppm) are shown in Table 3. It can be observed from the table that the corrosion rate of carbon steel in the absence of any inhibitor is very much higher in hydrodynamic conditions than in static conditions. Also, corrosion rate increases with increase in rotational speed. It is interesting to observe the excellent protection property of the inhibitor formulation in the hydrodynamic conditions. Further, highest inhibition efficiency of the formulation is retained at all the rotational speeds up to 900 rpm considered in the present study. These results infer the effectiveness of the inhibitor formulation in corrosion control even in hydrodynamic conditions that are maintained in industrial cooling water systems.

**Table 3. Corrosion rates of carbon steel in 200 ppm of NaCl in the absence and presence of the inhibitor formulation in static as well as in hydrodynamic conditions**

| Rotation speed (rpm) | Control | Inhibitor | |
|---|---|---|---|
| | Corrosion rate (mmpy) | Corrosion rate (mmpy) | I.E. (%) |
| **Static Conditions** | | | |
| 0 | 0.173256 | 0.002126 | 98.77 |
| **Hydrodynamic conditions** | | | |
| 300 | 0.770617 | 0.003188 | 99.58 |
| 600 | 1.173463 | 0.005314 | 99.54 |
| 900 | 1.643274 | 0.009566 | 99.41 |



## 4. Conclusions

1. The new ternary formulation, NTMP-$Zn^{2+}$-nicotonic acid, is an effective inhibitor for carbon steel in aqueous environment.
2. Nicotonic acid is an excellent synergist in combination with NTMP and $Zn^{2+}$ for corrosion inhibition.
3. The ternary inhibitor system is effective in the pH range 5 to 9.
4. Minimum dosage for maintenance of the protective film is found to be less than that required for the formation of protective film, which infers that the formulation is more environmentally friendly.
5. Good inhibition efficiency of the formulation is retained for longer immersion periods as well as in hydrodynamic conditions. This study reveals the possibility of applying the new ternary formulation for industrial applications.

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