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Nitrilotris(methylenephosphonic acid) – Zinc Ions – Uric Acid: A New Ternary Formulation as Corrosion Inhibitor for Carbon Steel

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Abstract— **A new ternary formulation containing Nitrilotris(methylenephosphonic acid) (NTMP), Zn^{2+} and uric acid (UA) is proposed as a new corrosion inhibitor for carbon steel in low chloride aqueous environment on the basis of the results obtained by gravimetric measurements. The concentration of Zn^{2+} in the formulation, required for effective an inhibition, could be reduced in presence of uric acid. The formulation is found to be effective in the pH range 4 to 9. The protective film formed by the inhibitor is stable for longer immersion periods and also under hydrodynamic conditions. Optimum concentrations of all the three components are found to be essential for both formation and maintenance of the protective film on the surface. The results of the present study reveal the strong synergistic effect existing among the three components of the inhibitor and infer the possibility of practical application of the inhibitor in cooling water systems.**

Keywords-NTMP; gravimetric studies; synergism; corrosion inhibition; carbon steel; uric acid

I. INTRODUCTION

Carbon steel is a very significant and commercially important material for industrial metallic constructions due to ease of fabrication and low cost. But one of the major challenges arrived at while using this material is susceptibility to undergo corrosion. Several phosphonate-based formulations were found to be effective corrosion inhibitors for carbon steel in low chloride aqueous environments through synergism [1-3]. However, these formulations demand higher concentrations of phosphonic acid as well as zinc ions for exhibiting good inhibition. But, according to the environmental guidelines, disposal of higher levels of Zn^{2+} in wastewaters from industries is objectionable. Hence, phosphonate-based formulations can further be applied for protection of carbon steel only if the concentration of zinc ions could be reduced to the permissible limits. Addition of one more synergist to phosphonate-Zn^{2+} binary systems may reduce the required concentration of Zn^{2+} for an effective inhibition. The synergist selected for this purpose is generally an environmentally friendly organic or inorganic compound so that the resulting formulations called ternary inhibitor formulations are more environmentally friendly. A few of such ternary formulations were already reported in literature [4-6]. In this background, a commercially important phosphonic acid namely Nitrilotris(methylenephosphonic acid) (NTMP) is chosen for the present study. It consists of three phosphonic acid groups which can participate in complex formation with metal ions like Zn^{2+}. Uric acid is chosen as the second synergist to NTMP-Zn^{2+} binary system. Uric acid is one of the major nitrogen containing excretory products in biological systems and is a naturally occurring antioxidant [7]. Uric acid is known to form complexes with metal ions like Fe^{3+} [8]. Uric acid contains four –NH groups which can participate in chelation with metal ions. In the present study, optimum concentrations of all the three components namely NTMP, Zn^{2+} and uric acid to achieve good inhibition efficiency, were determined. The effects of pH and hydrodynamic conditions on inhibition efficiency of the ternary formulation were determined. Dosages of inhibitor components required for maintenance of the protective film and effect of longer immersion periods on inhibition efficiency were also evaluated. The main objective of the present study is to introduce uric acid as a new synergist to the existing binary inhibitor formulation containing NTMP and zinc ions. Further, this study was started with an aim of examining the effectiveness of the new ternary formulation namely NTMP-Zn(II)-UA as corrosion inhibitor for carbon steel with reference to concentration of the components, pH of the environment, immersion time and hydrodynamic conditions. The entire study is limited to gravimetric method using 200 ppm of NaCl as the control. The study is limited to carbon steel.

II. EXPERIMENTAL

All the results reported in the present study are entirely obtained from 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 [9]. However, they require a long time for the determination of corrosion rates. For all the studies, the specimens taken from a single sheet of carbon steel with 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 emery polishing papers of the grades 1/0, 2/0, 3/0 and 4/0 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 ($ZnSO_4.7H_2O$), uric acid ($C_5H_4N_4O_3$) and other reagents were analytical grade chemicals. 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. 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 [10]. 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 hours in view of the lengthy immersion time of 168 hours. 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 hours [11]. 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,

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

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

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 7.0. Based on these concentrations, 20-40 ppm of NTMP and 10 ppm as well as 15 ppm of zinc ions were considered in combination with 10-80 ppm of uric acid. The influence of pH on inhibition efficiency of the effective ternary inhibitor formulation was also studied in the pH range, 3.0-10.0. 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 7.0 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.

III. Results and Discussion

A. Effect of 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 7.0 are presented in Fig. 1. From 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 this composition, the binary system afforded an inhibition efficiency (I.E.) of 97 %. It is expected that when the non-toxic organic additive namely uric acid is added to the binary system, it can considerably reduce the concentrations of both NTMP and Zn^{2+} required for an effective inhibition. Before proceeding for the determination of inhibition efficiency of the ternary inhibitor system, the synergist, uric acid alone was tested for its efficiency as a corrosion inhibitor. The results are shown in Fig. 2. It shows that the highest inhibition efficiency of uric acid alone is only 42 % at 400 ppm concentration. At still higher concentrations, the inhibition efficiency is found to be decreased. Fig. 3 shows the results of gravimetric studies of the ternary inhibitor system, NTMP (20-40 ppm) + Zn^{2+} (10-15 ppm) + uric acid (0-80 ppm) at pH 7.0. It can be observed from the figure that when uric acid is added to the combination of NTMP and Zn^{2+} of any concentration, inhibition efficiency increases with increase in concentration of uric 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 (40 ppm) and uric acid (10-80 ppm) exhibited negative inhibition efficiency values. From Fig. 3, it can be concluded that minimum concentrations of NTMP, Zn^{2+} and uric acid required for exhibiting highest inhibition efficiency (I.E.) of 97.7 %, are 40 ppm, 15 ppm and 20 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 reported that phosphonate-based inhibitor formulations are effective due to formation of protective surface films and that such films are composed of complexes of phosphonic acid with metal ions, Zn^{2+} [1-3].

B. Effect of pH

Fig. 4 shows the results of gravimetric studies of the effective inhibitor formulation at different pH values from 3.0 to 10.0. It indicates that the new ternary formulation is effective in the pH range 4.0 to 9.0. The concentration of uric acid required for effective inhibition in this pH range is 20-40 ppm. The pH range of water used in recirculating cooling water systems will not exceed 5.0-9.0. Hence, this inhibitor formulation is well suited for such systems as far as pH is concerned.

C. Maintenance dosages and effect of immersion period

It can be expected that the concentrations of the 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 uric acid required for the maintenance of the highest inhibition efficiency are 30, 5 and 10 ppm respectively. These results indicate that only 5 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. It is interesting to note from the table that the inhibition efficiency values of the inhibitor formulation with maintenance dosage are above 94 % 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.

D. Effect of hydrodynamic conditions

From the results of studies on effect of hydrodynamic conditions on inhibition efficiency of the ternary inhibitor formulation, NTMP (40 ppm) + Zn^{2+} (15 ppm) + UA (20 ppm), inhibition efficiencies of the inhibitor formulation were found to be 98.76 %, 98.60 %, 98.44 % and 98.43 % corresponding to rotational speeds 0, 300, 600 and 900 rpm respectively. Moreover, it was observed from the results 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.

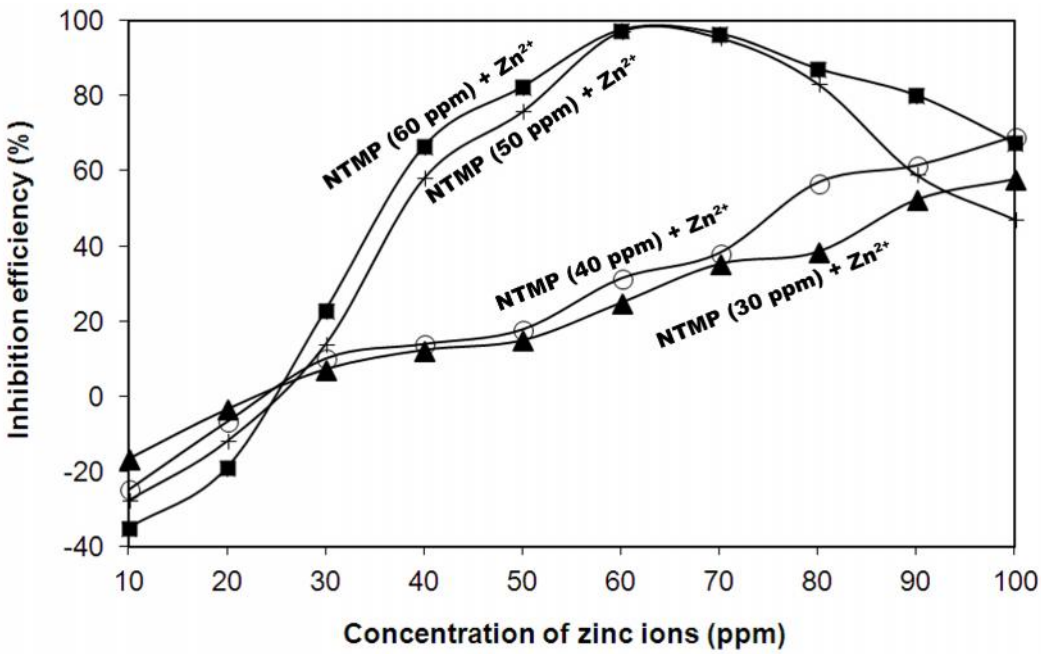

Figure 1. Corrosion inhibition efficiency of binary inhibitor system, NTMP-Zn^{2+} as a function of [Zn^{2+}] at pH = 7.0

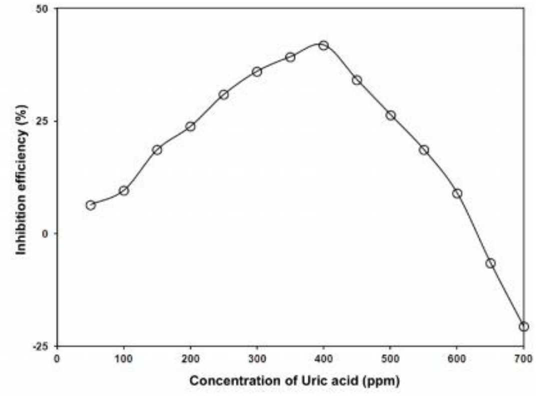

Figure 2. Corrosion inhibition efficiency of uric acid alone at pH = 7.0

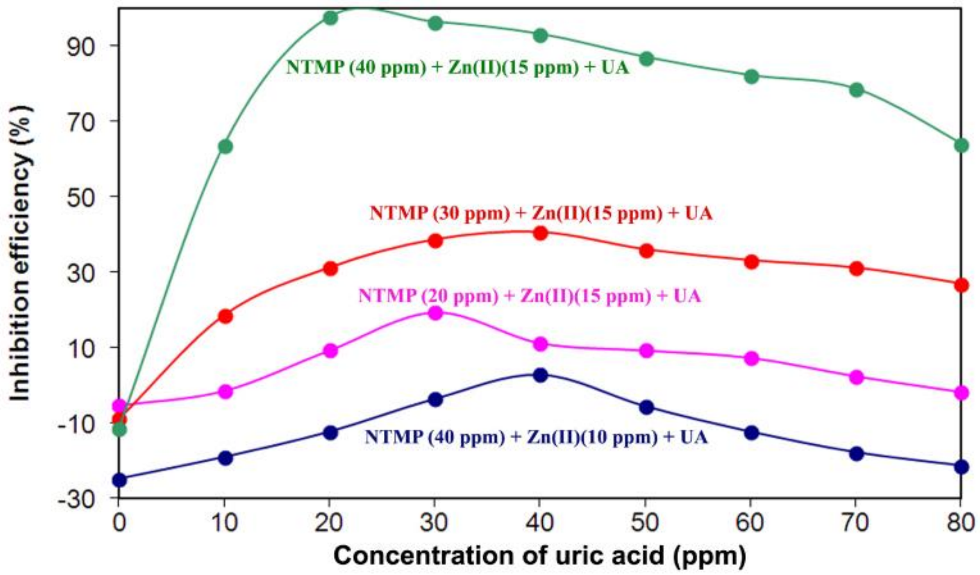

Figure 3. Corrosion inhibition efficiency of the ternary inhibitor system, NTMP – Zn^{2+} - UA, as a functionof [UA] at pH = 7.0

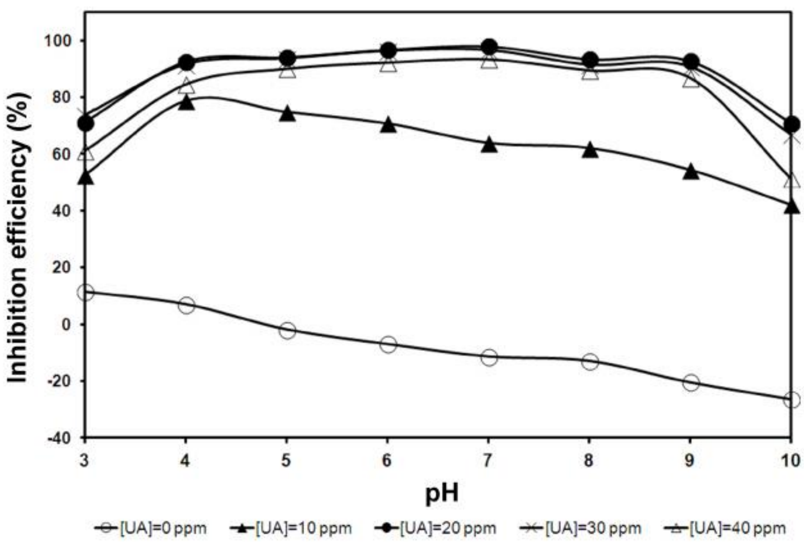

Figure 4. Corrosion inhibition efficiency of the ternary inhibitor system, NTMP (40 ppm) + Zn^{2+} (15 ppm) + UA, as a function of pH

TABLE I. RESULTS OF GRAVIMETRIC STUDIES OF THE INHIBITOR FORMULATIONS CONTAINING NTMP, ZINC IONS AND URIC ACID FOR MAINTENANCE OF THE PROTECTIVE FILM

S. No.	Maintenance dosage of the inhibitor components (ppm)			Corrosion rate (mmpy)	Inhibition efficiency (%)
	NTMP	Zn^{2+}	*Uric acid*		
1	0	0	0	0.070608	---
2	40	15	20	0.001594	97.74
3	40	10	20	0.001813	97.43
4	40	5	20	0.002590	96.33
5	30	5	20	0.003318	95.30
6	20	5	20	0.012497	82.30
7	10	5	20	0.016450	76.70
8	30	5	10	0.004092	94.20
9	30	5	0	0.022311	68.40

TABLE II. CORROSION RATES OF CARBON STEEL IMMERSED IN 200 PPM OF SODIUM CHLORIDE SOLUTION IN THE ABSENCE AND PRESENCE OF NTMP (30 PPM) + ZINC IONS (5 PPM) + URIC ACID (10 PPM) AT DIFFERENT IMMERSION PERIODS

S. No.	Immersion period (days)	Control (200 ppm NaCl)		Inhibitor formulation	
		Corrosion rate (mmpy)	*Inhibition efficiency (%)*	*Corrosion rate (mmpy)*	*Inhibition efficiency (%)*
1	7	0.070608	---	0.004092	94.20
2	14	0.070722	---	0.002847	95.97
3	21	0.071974	---	0.002429	96.62
4	28	0.073110	---	0.002278	96.88
5	35	0.073250	---	0.002141	97.07
6	42	0.075277	---	0.001974	97.38
7	49	0.075261	---	0.001984	97.40
8	56	0.079035	---	0.002050	97.40
9	63	0.081920	---	0.002227	97.28

IV. CONCLUSIONS

The ternary inhibitor formulation, NTMP–Zn(II)–uric acid, is an effective corrosion inhibitor for carbon steel in low chloride aqueous environment. Uric acid is an excellent synergist to the binary system, NTMP-Zn(II), in corrosion control. The new ternary formulation is found to be effective in the pH range, 4.0 to 9.0. The required optimum concentrations of the inhibitor components for maintenance of the protective nature are less than those required for formation of protective film. Only 5 ppm of Zn^{2+} is sufficient to maintain the protection behaviour, thus, making the formulation more environmentally friendly. In addition, the inhibition efficiency is maintained for longer immersion periods of even up to 63 days. The formulation is equally effective in both static and hydrodynamic conditions, which favours its usage for industrial applications.

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