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RESEARCH ARTICLE

SYNERGISTIC EFFECT OF FOLIC ACID ON CORROSION INHIBITION OF CARBON STEEL IN PRESENCE OF A PHOSPHONATE AND ZINC IONS

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ABSTRACT

Folic acid (FA), a non-toxic organic compound, is introduced as a synergist to the combination of nitrilotris(methylenephosphonic acid) (NTMP) and zinc ions. Results of gravimetric studies on the protective nature of surface film produced by the new ternary formulation, NTMP, zinc ions and folic acid on carbon steel in low chloride aqueous environment are presented. The surface film could be produced at relatively low concentrations of both NTMP and Zn^{2+} in presence of folic acid, when compared with the binary system containing only NTMP and Zn^{2+}. The required minimum concentration of Zn^{2+} for maintenance of the protective film is found to be only 15 ppm. The new ternary inhibitor formulation is effective in the pH range 5 to 9. The protective nature of the surface film is retained for longer immersion periods as well as in hydrodynamic conditions.

INTRODUCTION

Application of corrosion inhibitors is one among the effective methods for controlling corrosion of commercial materials like carbon steel in cooling water systems, heat exchangers, etc. Since past three decades, phosphonate-based formulations have gained great importance as corrosion inhibitors in such systems. Predominance of phosphonates as corrosion inhibitors is due to their ability to produce bonds with metal ions like Zn^{2+} to form stable complexes. These complexes play very significant role in making the metal surface film protective. Several studies on phosphonate-Zn^{2+} binary formulations were reported in literature, proving them to be effective corrosion inhibitors for carbon steel in aqueous environments (Amar *et al.*, 2003; Awad and Turgoose, 2004; Demadis *et al.*, 2005; Fang *et al.*, 1993; Felhosi *et al.*, 1999; Gonzalez *et al.*, 1996; Nakayama, 2000; Ochoa *et al.*, 2002; Pech-Canual and Bartolo-Perez, 2004; Pech-Canul and Chi-Canual, 1999; Reznik *et al.*, 2008; Shaban *et al.*, 1993; Sekine and Hirakawa, 1986 and Telegdi *et al.*, 2001). However, these formulations demand higher concentrations of both the components, particularly zinc ions. According to the environmental guidelines, disposal of wastewaters with higher levels of toxic components like zinc ions, is restricted. In order to overcome this demerit in the applicability of phosphonate-based binary inhibitor formulations, another non-toxic organic or inorganic compound can be added to the binary systems. The resulting formulations are termed as ternary inhibitor formulations which also control corrosion of carbon steel as effectively as the binary formulations but at relatively low concentrations of both phosphonate and zinc ions. A few reports are available on ternary inhibitor formulations which protect the metal based on the synergistic action among the three inhibitor components (Appa Rao *et al.*, 2008; Appa Rao *et al.*, 2013 and Appa Rao and Srinivasa Rao, 2010).

In this background, a new ternary inhibitor formulation based on phosphonates is proposed in the present study. For this purpose, the selected phosphonic acid and the organic additive are nitrilotris(methylenephosphonic acid) (NTMP) and folic acid (FA) respectively. NTMP is one of the phosphonates used on a large scale in industrial cooling water systems and oilfield water pipeline in thermal power plants and oil refinery plants (Kolodynska *et al.*, 2013). Folic acid is a non-toxic organic compound. It is vitamin-B_9 essential for numerous bodily functions. This compound is essential to produce healthy red

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blood cells and prevent anaemia. Folic acid is also known to form complexes with metal ions (Sekine *et al.*, 1988), which is due to presence of several functional groups like carboxylic acid groups, –NH moieties and heterocyclic nitrogen atoms. The main objective of the present study is to investigate the effectiveness of the ternary inhibitor formulation containing namely NTMP, Zn^{2+} and FA in corrosion control of carbon steel through synergism in nearly neutral aqueous chloride environment. For the present study, 200 ppm of NaCl solution has been chosen as control 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.

MATERIALS AND METHODS

The specimens taken from a single sheet of carbon steel of the following composition were chosen for the present study. 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 of the dimensions, 3.5 cm x 1.5 cm x 0.2 cm, 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. NTMP ($C_3H_{12}NO_9P_3$), Zinc sulphate ($ZnSO_4.7H_2O$), folic acid ($C_{12}H_{22}O_{12}$) and other reagents were AnalaR grade chemicals. Molecular structures of NTMP and folic acid (FA) are shown in Fig. 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.

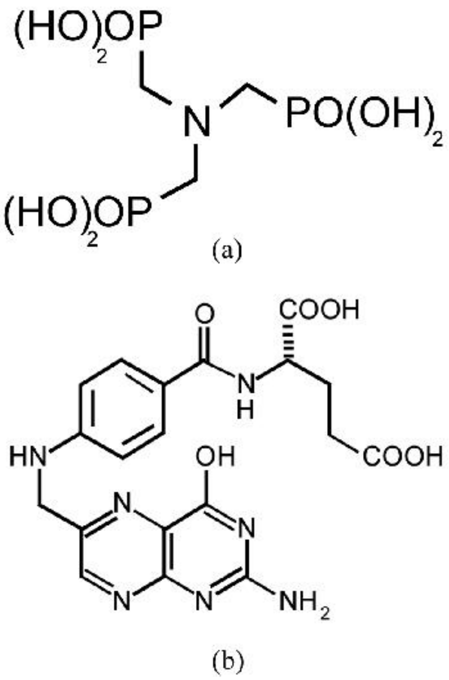

Figure 1 Structures of inhibitor molecules (a) NTMP and (b) Folic acid

In all the gravimetric experiments, 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 (ASTM Standard G31-72). 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 (Freeman and Silverman, 1992).

Corrosion rates (CR) of carbon steel in the absence and presence of various inhibitor formulations are expressed 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.

Gravimetric studies of the binary formulations containing NTMP (30-60 ppm) and Zn^{2+} (10-100 ppm) carried out in order to determine the minimum concentrations of both the components required for an effective inhibition were presented elsewhere (Sarada Kalyani *et al.*, 2012) by the authors of the present study. Based on the results of these studies, gravimetric studies were carried out, in the present study, considering the ternary inhibitor formulations, NTMP (20-40 ppm), Zn^{2+} (15-20 ppm) and FA (10-80 ppm) at pH 7. The influence of pH on inhibition efficiency of the effective ternary inhibitor formulations 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 decide 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. 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.

RESULTS AND DISCUSSION

Figure 2 shows the results of gravimetric studies carried out by considering folic acid alone as a corrosion inhibitor. These results indicate that folic acid alone cannot act as an effective corrosion inhibitor for carbon steel. The highest inhibition efficiency of only 45.81 % could be achieved by folic acid at the concentration of 500 ppm. Figure 3 shows the results of gravimetric studies of the ternary inhibitor system, NTMP (20-40 ppm) + Zn^{2+} (15-20 ppm) + FA (0-80 ppm) at pH = 7. The selected concentration ranges of both NTMP and Zn^{2+} in these formulations are based on the results of gravimetric studies of the binary inhibitor formulation (Sarada Kalyani *et al.*, 2012), which indicated that the minimum concentrations of NTMP and Zn^{2+} required for an effective inhibition efficiency of 97 % are 50 ppm and 60 ppm respectively. It can be observed from Fig. 3 that when folic acid is added to the combination of NTMP and Zn^{2+} of any concentration, inhibition efficiency increases with increase in concentration of folic 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 folic acid (0-80 ppm) exhibited negligible values of inhibition efficiency. These results are not included in the figure. From Fig. 3, it can be concluded that minimum concentrations of NTMP, Zn^{2+} and folic acid required for exhibiting highest inhibition efficiency (I.E.) > 96 %, are 30 ppm, 20 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. Literature reports reveal 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 (Felhosi *et al.*, 1999; Gonzalez *et al.*, 1996 and Demadis *et al.*, 2006). It may also be noted that even at higher concentration of NTMP at 40 ppm, and folic acid concentrations up to 80 ppm, good inhibition efficiency could not be achieved when the concentration of Zn^{2+} is less than 20 ppm.

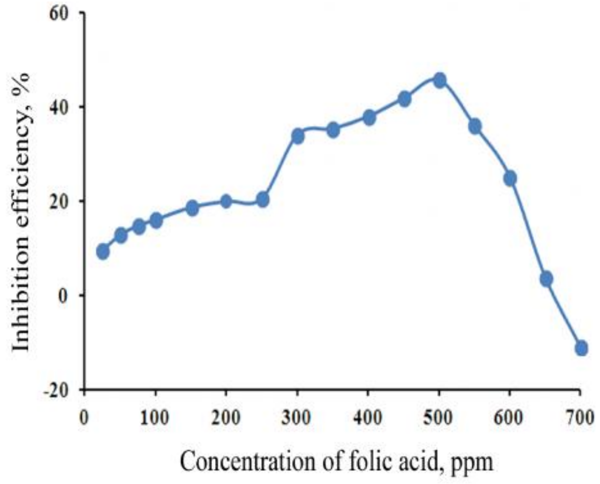

Figure 2 Corrosion inhibition efficiency of folic acid alone at different concentrations

While the binary system consisting of 30 ppm of NTMP and 20 ppm of Zn^{2+} slightly aggravated corrosion of carbon steel, the ternary inhibitor system containing 20 ppm of FA along with 30 ppm of NTMP and 20 ppm of Zn^{2+}, afforded an inhibition efficiency of 96.44 %. The synergistic effect of folic acid in the ternary system is established by this result. However, at higher concentrations of FA such as 70 and 80 ppm, the inhibition efficiency is reduced to 59.67 % and 50.32 % respectively. From these results, it can be observed that in case of all the ternary inhibitor formulations, as the concentration of FA is increased, the corrosion rate decreases, reaches a minimum at an optimum concentration of FA and then increases. Thus, the mixture containing optimum concentrations of each of the components gives the highest inhibition efficiency. In other words, optimum amounts of each of the three components must be available in the solution, so that each one of them plays its own synergistic role in the formation of protective film covering the entire metal surface. It may be mentioned here that the molar ratio of NTMP : Zn^{2+} : FA is 1 : 3.0 : 0.5 to exhibit excellent synergism with the highest inhibition efficiency of 96.44 %.

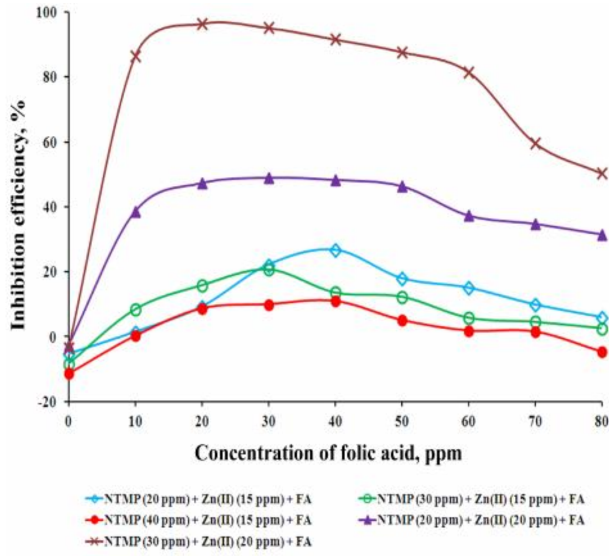

Figure 3 Corrosion inhibition efficiency of ternary inhibitor system, NTMP (20-40 ppm) + Zn^{2+} (15-20 ppm) + FA, as a function of concentration of folic acid

The influence of pH on inhibition efficiency of the inhibitor system namely, NTMP (30 ppm) + Zn^{2+} (20 ppm) + FA (0-40 ppm), in the pH range of 4.0-10.0, is shown in Fig. 4. The highest inhibition efficiency could be obtained by the formulation containing NTMP (30 ppm) + Zn^{2+} (20 ppm) + FA (20-30 ppm) in the pH range of 5.0-9.0.

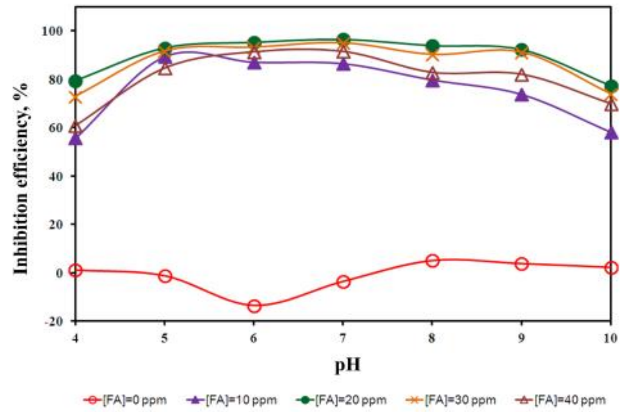

Figure 4 Corrosion inhibition efficiency of the inhibitor system, NTMP (30 ppm) + Zn^{2+} (20 ppm) + FA (0-40 ppm), as a function of pH

But if the pH is either decreased from 5.0 to 4.0 or increased from 9.0 to 10.0, the inhibition efficiency is reduced. Nevertheless, in cooling water systems, water used is nearly neutral i.e., pH is generally maintained between 6.0 and 8.0. Hence, the ternary system, NTMP–Zn^{2+}–FA, is an effective inhibitor for cooling water systems as far as the effect of pH is considered.

The results of gravimetric studies carried out in order to determine the minimum concentrations of all the three components of the inhibitor formulation for maintenance of the protective film are shown in Table 1. The results indicate that the inhibitor mixture containing only 20 ppm of NTMP, 15 ppm of Zn^{2+} and 10 ppm of FA could maintain the protective film. The maintenance dosage of NTMP : Zn^{2+} : FA in terms of molar ratio is 1 : 3.5 : 0.4.

Table 1 Results of gravimetric studies of the inhibitor formulations containing NTMP, zinc ions and folic acid for maintenance of the protective film

Maintenance dosage of the inhibitor components (ppm)			Corrosion rate (mmpy)	Inhibition efficiency (%)
NTMP	Zn^{2+}	FA		
0	0	0	0.070608	---
30	20	20	0.002505	96.45
30	15	20	0.003260	95.38
30	10	20	0.009174	87.00
30	5	20	0.015032	78.71
20	15	20	0.003417	95.16
10	15	20	0.018690	73.52
20	15	10	0.003702	94.75
20	15	0	0.022501	68.13

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 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.

Table 2 Corrosion rates of carbon steel immersed in control solution in the absence and presence of the maintenance dosage at different immersion periods

Immersion period (days)	Control (200 ppm NaCl)		Inhibitor formulation	
	Corrosion rate (mmpy)	IE (%)	Corrosion rate (mmpy)	IE (%)
7	0.070608	---	0.003702	94.75
14	0.070722	---	0.002619	96.29
21	0.071974	---	0.002126	97.05
28	0.073110	---	0.001879	97.43
35	0.073250	---	0.001958	97.32
42	0.075277	---	0.001898	97.48
49	0.075261	---	0.001789	97.62
56	0.079035	---	0.001651	97.91
63	0.081920	---	0.001696	97.93

The results of studies on effect of hydrodynamic conditions on inhibition efficiency of the ternary inhibitor formulation, NTMP (30 ppm) + Zn^{2+} (20 ppm) + FA (20 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, as inferred by the inhibition efficiency > 98 %. Further, the 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 immersed in control solution in the absence and presence of inhibitor formulation in both static and hydrodynamic conditions (Immersion period = 3 days)

Rotation speed (rpm)	Control (200 ppm NaCl)		Inhibitor formulation	
	Corrosion rate (mmpy)	IE (%)	Corrosion rate (mmpy)	IE (%)
0	0.173256	---	0.003221	98.14
300	0.770617	---	0.011812	98.46
600	1.173463	---	0.019328	98.35
900	1.643274	---	0.027919	98.30

CONCLUSIONS

The following conclusions are drawn from the present investigation:

1. Folic acid, a non-toxic organic compound, is proved to be an excellent synergist in the combination of NTMP and Zn^{2+} for corrosion control of carbon steel in nearly neutral aqueous environment.
2. The ternary formulation containing 30 ppm of NTMP and 20 ppm of Zn^{2+} along with 20 ppm of folic acid is an effective corrosion inhibitor for carbon steel. Once the protective film is formed, a mixture of 20 ppm of NTMP, 15 ppm of Zn^{2+} and 10 ppm of folic acid will serve as the maintenance dosage. The ternary inhibitor system is, thus, relatively more environmentally friendly.
3. The protective film is maintained with the maintenance dosage for longer immersion periods up to 63 days.
4. The inhibitor formulation is effective in the hydrodynamic conditions also. The inhibitor system works in the pH range 5-9.

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