Chemical Science Review and Letters ISSN 2278-6783

Research Article

Effect of Various Factors on Corrosion Inhibition of Carbon Steel Using a Phosphonate-Based Inhibitor System

D. Sarada Kalyani, and S. Srinivasa Rao*

Department of Chemistry, V. R. Siddhartha Engineering College (Autonomous), Vijayawada-520007, Andhra Pradesh, India

Abstract

A ternary formulation consisting of 1-hydroxyethane-1,1-diphosphonic acid (HEDP), Zn(II) and folic acid (FA), is introduced as an inhibitor for corrosion control of carbon steel in aqueous chloride environment. Results of gravimetric studies showed that this new inhibitor is highly effective in corrosion control due to synergistic action existing among the inhibitor components. The highest inhibition efficiency of 96 % was achieved by the formulation containing 40 ppm of HEDP, 20 ppm of Zn^{2+} and 20 ppm of FA. The inhibition efficiency is maintained at still lower concentrations of the inhibitor components, making the inhibitor more environmentally friendly. Moreover, such high inhibition efficiency was maintained for longer immersion periods. The formulation is found to be effective in the pH range 4.0-9.0. The formulation showed excellent inhibition in hydrodynamic conditions also. These studies inferred that FA acts as a good synergist to HEDP-Zn(II) system in corrosion inhibition of carbon steel.

Correspondence
S. Srinivasa Rao,
Email: Chemsri@yahoo.com

Keywords Carbon steel, Phosphonate, Synergism, Inhibition efficiency, Gravimetric studies.

Introduction

Among several metallic construction materials, carbon steel is a very significant and commercially used material 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. The concept of synergism can again help to handle this task. 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 1-hydroxyethane-1,1-diphosphonic acid (HEDP) is chosen for the present study. It consists of two phosphonic acid groups which can participate in complex formation with metal ions like Zn^{2+}. Folic acid is chosen as the second synergist to HEDP-Zn^{2+} binary system. Folic acid is an environmentally friendly organic compound. It is vitamin-B_9 essential for numerous bodily functions and it is essential to produce healthy red blood cells and prevent anemia. It consists of aromatic heterocyclic rings with nitrogen atoms, –NH moieties, amino and hydroxyl groups and two carboxylic acid groups. This molecule is known to form complexes with metal ions [7]. In the present study, optimum concentrations of all the three components namely HEDP, Zn^{2+} and folic 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.

Experimental

All the results reported 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 [8]. 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 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. HEDP ($C_2H_8O_7P_2$), Zinc sulphate ($ZnSO_4.7H_2O$), folic acid ($C_{19}H_{19}N_7O_6$) and other reagents were analytical grade chemicals. Molecular structures of HEDP and folic 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 [9]. 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 [10]. 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.

Gravimetric studies were carried out using binary inhibitor formulation, HEDP-Zn^{2+}, in order to determine the required minimum concentrations of both HEDP and Zn^{2+} for an effective inhibition at pH 7.0. Based on these concentrations, 30-50 ppm of HEDP and 15 ppm as well as 20 ppm of zinc ions were considered in combination with 10-80 ppm of folic 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.

Results and Discussion

Effect of concentrations of the inhibitor components

Results of gravimetric studies of corrosion inhibition of carbon steel using the binary inhibitor system, HEDP-Zn^{2+}, at pH 7.0 are presented in **Figure 2**. From figure, it can be inferred that the minimum concentrations of HEDP and Zn^{2+} required for an effective inhibition are 60 ppm and 50 ppm respectively. With this composition, the binary system afforded an inhibition efficiency (I.E.) of 95 %. It is expected that when the non-toxic organic additive namely folic acid is added to the binary system, it can considerably reduce the concentrations of both HEDP and Zn^{2+} required for an effective inhibition. Before proceeding for the determination of inhibition efficiency of the ternary inhibitor system, the synergist, folic acid alone was tested for its efficiency as a corrosion inhibitor. The results are shown in **Figure 3**. It shows that the highest inhibition efficiency of folic acid alone is only 46 % at 500 ppm concentration. At still higher concentrations, the inhibition efficiency is found to be decreased. **Figure 4** shows the results of gravimetric studies of the ternary inhibitor system, HEDP (30-50 ppm) + Zn^{2+} (15-20 ppm) + folic acid (0-80 ppm) at pH 7.0. It can be observed from the figure that when folic acid is added to the combination of HEDP 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 formulations containing 10 ppm of Zn^{2+} along with HEDP (30-50 ppm) and folic acid (10-80 ppm) exhibited very low inhibition efficiency values.

From Figure 4, it can be concluded that minimum concentrations of HEDP, Zn^{2+} and folic acid required for exhibiting highest inhibition efficiency (I.E.) of 95.8 %, are 40 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. 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 complexes of phosphonic acid with metal ions, Zn^{2+} [1-3,11].

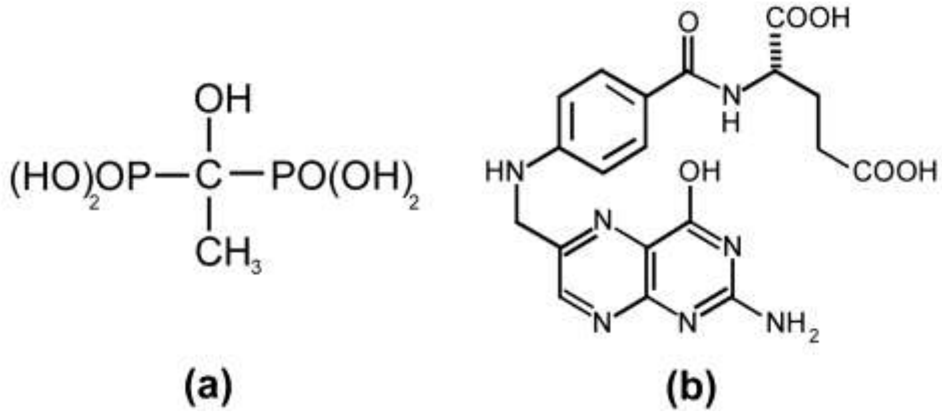

Figure 1 Molecular structures of the inhibitor components (a) HEDP; (b) Folic acid

Effect of pH

Figure 5 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 folic acid required for effective inhibition in this pH range is 20-30 ppm. With 40 ppm of folic acid in the ternary inhibitor formulation, the inhibition efficiency is found to be slightly less than 90 %. 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.

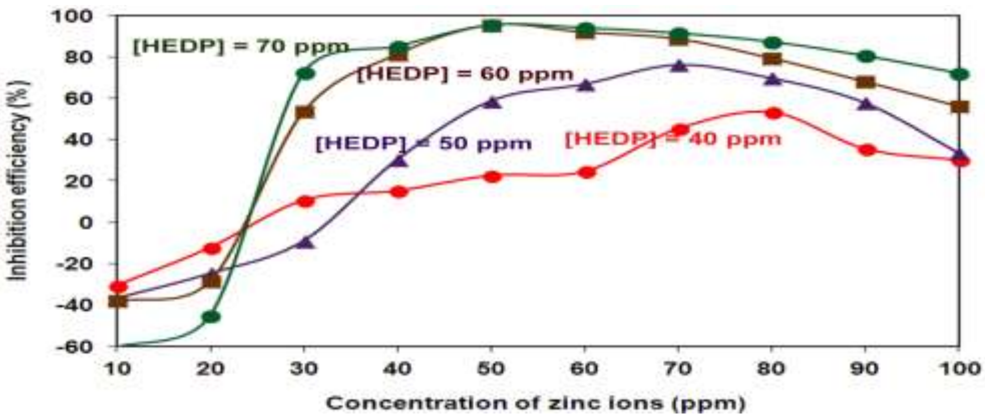

Figure 2 Corrosion inhibition efficiency of binary inhibitor system, HEDP-Zn^{2+} as a function of [Zn^{2+}] at pH 7.0

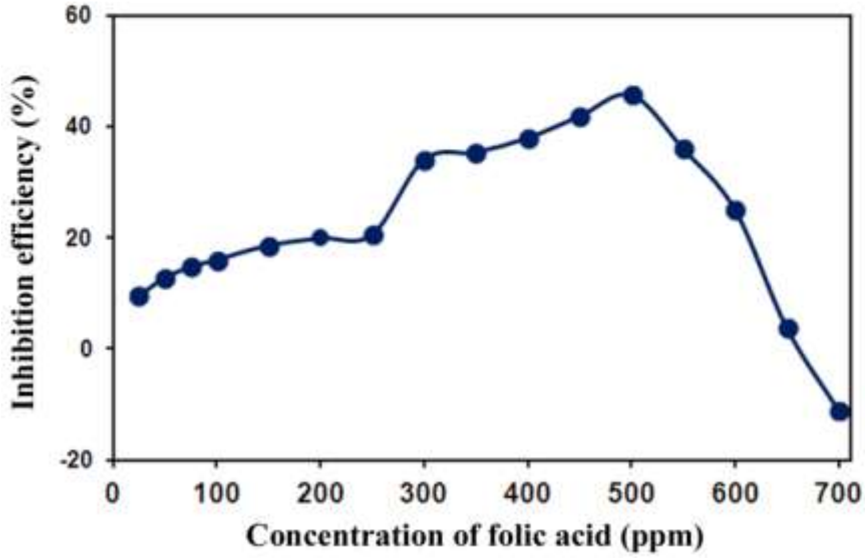

Figure 3 Effect of folic acid concentration on IE%

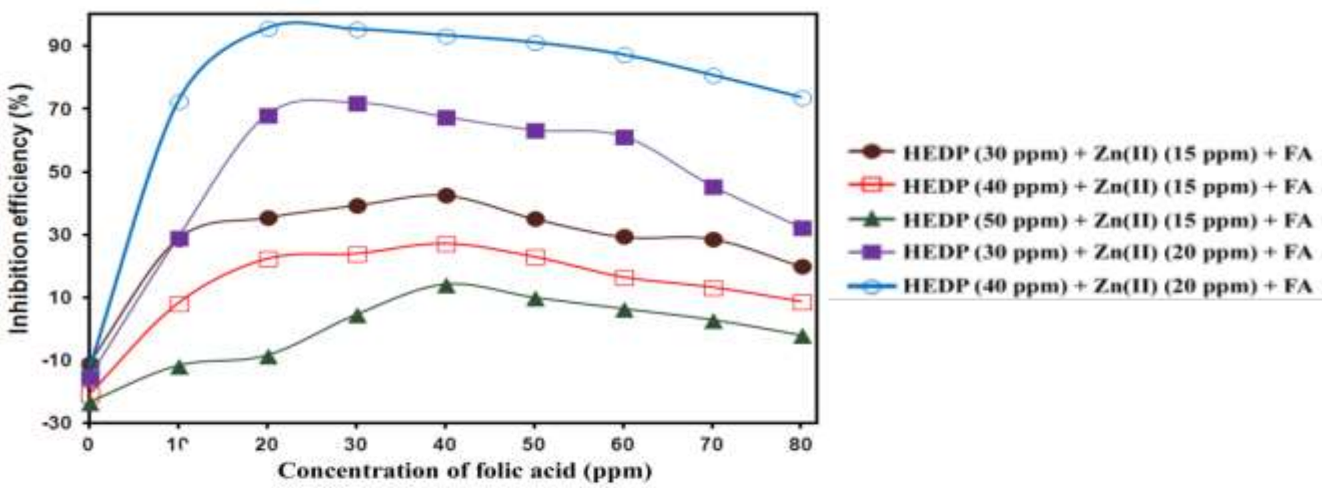

Figure 4 Corrosion inhibition efficiency of the ternary inhibitor system, HEDP-Zn^{2+}-FA, as a function of concentration of folic acid at pH 7.0

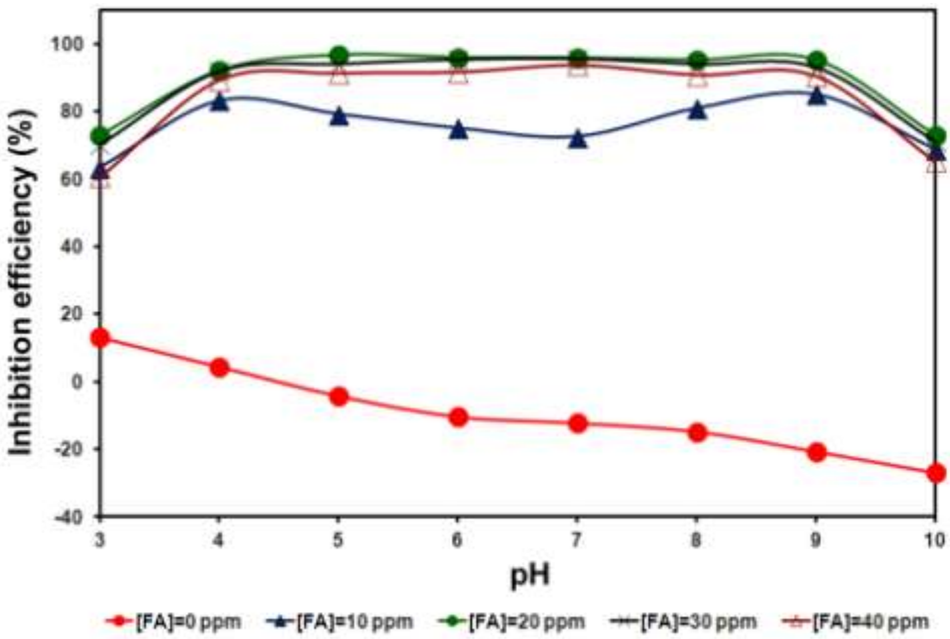

Figure 5 Corrosion inhibition efficiency of the ternary inhibitor system, HEDP (40 ppm)-Zn^{2+} (20 ppm)-FA, as a function of pH

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 95.8 % 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 HEDP, Zn^{2+} and folic acid required for the maintenance of the highest inhibition efficiency are 30, 10 and 10 ppm respectively.

These results indicate that only 10 ppm of Zn^{2+} is sufficient to maintain the protective nature of the surface film. Hence, the ternary formulation is more environmentally friendly than HEDP-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 93 % 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.

Effect of hydrodynamic conditions

The results of studies on effect of hydrodynamic conditions on inhibition efficiency of the ternary inhibitor formulation, HEDP (40 ppm) + Zn^{2+} (20 ppm) + folic acid (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. 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 1 Results of gravimetric studies of the inhibitor formulations containing HEDP, Zn^{2+} and folic acid for maintenance of the protective film

S. No.	Maintenance dosage of the inhibitor components (ppm)			Corrosion rate (mmpy)	Inhibition efficiency (%)
	HEDP	Zn^{2+}	Folic acid		
1	0	0	0	0.070608	---
2	40	20	20	0.002961	95.80
3	40	15	20	0.003178	95.49
4	40	10	20	0.003857	94.53
5	40	5	20	0.011618	83.54
6	30	10	20	0.004104	94.18
7	20	10	20	0.014271	79.78
8	10	10	20	0.025877	63.35
9	30	10	10	0.004812	93.18
10	30	10	0	0.027940	60.43

Table 2 Corrosion rates of carbon steel immersed in 200 ppm of NaCl solution in the absence and presence of HEDP (30 ppm) + Zn^{2+} (10 ppm) + folic 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	---	0.004812	93.18
2	14	0.070722	---	0.002961	95.81
3	21	0.071974	---	0.002354	96.73
4	28	0.073110	---	0.002221	96.96
5	35	0.073250	---	0.002004	97.26
6	42	0.075277	---	0.001898	97.48
7	49	0.075261	---	0.001822	97.58
8	56	0.079035	---	0.001679	97.87
9	63	0.081920	---	0.001721	97.90

Table 3 Corrosion rates of carbon steel immersed in 200 ppm of NaCl solution in the absence and presence of HEDP (40 ppm) + Zn^{2+} (20 ppm) + folic acid (20 ppm) with an immersion period of 3 days in both static as well as hydrodynamic conditions

S. No.	Rotation speed (rpm)	Control (200 ppm NaCl)		Inhibitor formulation	
		Corrosion rate (mmpy)	I. E. (%)	Corrosion rate (mmpy)	I. E. (%)
1	0	0.173256	---	0.003221	98.14
2	300	0.770617	---	0.007517	99.02
3	600	1.173463	---	0.011812	98.99
4	900	1.643274	---	0.016107	99.01

Conclusions

The ternary inhibitor formulation, HEDP – Zn(II) – folic acid, is an effective corrosion inhibitor for carbon steel in low chloride aqueous environment. Folic acid is an excellent synergist to the binary system, HEDP-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 10 ppm of Zn^{2+} is sufficient to maintain the protection behavior, 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.

References

[1] Gonzalez Y, Lafont M C, Pebere N, Moran F (1996) Synergistic effect between zinc salt and phosphonic acid for corrosion inhibition of a carbon steel. J Appl Electrochem 26:1259-1265.

[2] Demadis K D, Chris Mantzaridis, Panagiotis Lykoudis (2006) Effects of structural differences on metallic corrosion inhibition by Meal-Polyphosphonate thin films. Ind Eng Chem Res 45:7795-7800.

[3] Felhosi I, Keresztes Zs, Karman F H, Mohai M, Bertoti I, Kalman E (1999) Effects of bivalent cations on corrosion inhibition of steel by 1-Hydroxyethane-1,1-diphosphonic acid. J Electrochem Soc 146:961-969.

[4] Appa Rao B V, Venkateswara Rao M, Srinivasa Rao S, Sreedhar B (2010) Tungstate as a synergist to phosphonate-based formulation for corrosion control of carbon steel in nearly neutral aqueous environment. J Chem Sci 122:639-649.

[5] Appa Rao B V, Venkateswara Rao M, Srinivasa Rao S, Sreedhar B (2013) "N,N-bis(phosphonomethyl) glycine, Zn^{2+} and tartrate" – A new ternary inhibitor formulation for corrosion control of carbon steel. Int J Mater Chem 3:17-27.

[6] Appa Rao B V, Srinivasa Rao, Sarath Babu M (2005) Synergistic effect of NTMP, Zn^{2+} and ascorbate in corrosion inhibition of carbon steel. Indian J Chem Technol 12:629-634.

[7] Sekine I, Nakahata Y, Tanabe H (1988) The corrosion inhibition of mild steel by ascorbic and folic acids. Corros Sci 28:987-1001.

[8] Singley J E, Beaudet B A, Markey P H, DeBerry D W, Kidwell J R, Malish D A, Corrosion Prevention and Control in Water Treatment and Supply Systems, Noyes Publications, New Jersey, USA, 1985.

[9] ASTM Standard G31-72, Standard Practice for Laboratory Immersion Corrosion Testing of Materials (Reapproved 1990), Annual Book of ASTM Standards, 0302, Philadelphia, PA:ASTM, 1990.

[10] Freeman R A, Silverman D C (1992) Error propagation I coupon immersion tests. Corrosion 48:463-466.

[11] Demadis K D, Christos Mantzaridis, Raptis R G, Mezei G (2005) Metal-organotetraphosphonate inorganic-organic hybrids: Crystal structure and anticorrosion effects of zinc hexamethylenediaminetetrakis(methylene-phosphonate) on carbon steels. Inorg Chem 44:4469-4471.

Publication History

Received 19th Sep 2013
Revised 20th Oct 2013
Accepted 28th Oct 2013
Online 08th Jan 2014