The role of phosphonates as transporters of Zn^{2+} ions in the inhibition of carbon steel in neutral solutions containing chlorides

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Keywords

Corrosion inhibitors, Acids, Steel

Abstract

Phosphonates have shown synergistic effects in combination with Zn^{2+} ions in controlling the corrosion of carbon steel immersed in neutral aqueous environments containing 60-ppm Cl^-. The role of phosphonates in the presence of Zn^{2+} ions has been investigated by polarisation tests and weight loss results. It was observed that the phosphonates functioned as transporters of Zn^{2+} ions from the bulk of the solution towards the metal surface. The phosphonate-Zn^{2+} bond is sufficiently strong to carry Zn^{2+} ions from the bulk solution towards the metal surface, but is weak enough for them to break to form a phosphonate-Fe^{2+} bond at anodic sites on the metal surface. Inhibition efficiency increases when the phosphonate-Zn^{2+} complex remains in solution in soluble form. Inhibition efficiency decreased when the phosphonate-Zn^{2+} complex was precipitated in the bulk of the solution.

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Introduction

Prior to the 1960s, inorganic corrosion inhibitors such as chromate, polyphosphate and nitrite, were used for the protection of carbon steel in aqueous media. Though they provided a reliable measure of corrosion protection, the discharge of toxic materials was considered unacceptable due to environmental safety guidelines.

Between 1960 and 1980, in addition to polyphosphates, phosphonates, phosphonocarboxylic acids and polymers were used as inhibitors in neutral aqueous media.

Phosphonic acids have been extensively used as corrosion inhibitors, due to their hydrolytic stability, ability to form complexes with metal ions, and scale-inhibiting properties (Chiesa *et al.*, 1985; Dupart *et al.*, 1985; Fang *et al.*, 1993; Felhosi *et al.*, 1999; Gonzalez *et al.*, 1996; Kuznetsov, 1990; Rajendran *et al.*, 2000; Rodin *et al.*, 1987; Sekine and Hirakawa, 1986; Zanzucchi and Thomas, 1988; Zhu and Zhou, 1989). They show synergistic effects in combination with Zn^{2+} ions.

The mutual influence of a phosphonate and Zn^{2+} in a phosphonate-Zn^{2+} system is an interesting area, which merits investigation in detail. Better inhibition efficiency is noticed when the phosphonate-Zn^{2+} complex remains in soluble form, i.e. in solution. On the other hand, when the phosphonate-Zn^{2+} complex is precipitated in the bulk of the solution, the inhibition efficiency decreases (Chiesa *et al.*, 1985). The phosphonate-Zn^{2+} bond must be strong enough to carry Zn^{2+} from the bulk of the solution towards the metal surface, yet weak enough to break on the metal surface to form the phosphonate-Fe^{2+} complex on the anodic sites of the metal surface.

The role of phosphonates as transporters of Zn^{2+} ions from the bulk of the solution towards the metal surface is considered in this paper, using polarisation and weight-loss studies. The influence of the size of the Fe^{2+}-phosphonate complex and the "Zn^{2+} transporting ability" of phosphonates on corrosion inhibition has also been investigated.

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Experimental

Preparation of the specimens

Carbon steel specimens (0.02 to 0.03% S, 0.03 to 0.08% P, 0.4 to 0.5% Mn, 0.1 to 0.2% C and the balance iron) of the dimensions 40 × 10 × 2mm were polished to a mirror finish, degreased with trichloroethylene, and used for weight-loss tests and surface examination studies. For potentiostatic polarisation studies, carbon steel rod encapsulated in Teflon, with an exposed cross-section of 5mm diameter, was used as the working electrode. The working surface was polished to a mirror finish and was degreased with trichloroethylene.

Weight-loss tests

Three carbon steel specimens were immersed in 10ml of the neutral aqueous test solutions (with a chloride content of 60ppm) containing various concentrations of the inhibitors [aminotrimethylene phosphonic acid (ATMP), and 1-hydroxyethane-1,1-diphosphonic acid (HEDP)], in the absence and presence of Zn^{2+} ions (as $ZnSO_4.7H_2O$), for a period of seven days. After exposure, corrosion products were removed with Clarke's solution (Wranglen, 1985), and the weights of the specimens before and after immersion were determined using a Mettler balance, type AE-240.

The inhibition efficiency (IE) was calculated using the relation:

$$IE = 100[1 - (W_2/W_1)]\%$$

where: W_1 = Corrosion rate in the absence of inhibitor and: W_2 = Corrosion rate in the presence of inhibitor.

Potentiostatic polarisation studies

The polarisation studies were carried out in a three-electrode cell assembly, using carbon steel as the working electrode, platinum as the counter-electrode and saturated calomel electrode as the reference electrode. The cell was connected to a BioAnalytical Systems (BAS – 100A) electrochemical analyser with an iR compensation facility.

Results and discussion

Phosphonates, if used by themselves, are not good corrosion inhibitors. Nevertheless, they exhibit better inhibition efficiency on carbon steel (exposed in a neutral aqueous environment with 60ppm chloride ions) when used in combination with Zn^{2+}, due to the synergistic effect of the zinc ions. The mechanism of corrosion inhibition is as follows:

(1) When carbon steel is immersed in the neutral aqueous environment containing 60ppm Cl^-, the anodic reaction is:

$$Fe \rightarrow Fe^{2+} + 2e^-$$

and the cathodic reaction is:

$$2\ H_2O + O_2 + 4e^- \rightarrow 4\ OH^-.$$

(2) When an environment consisting of phosphonic acid and Zn^{2+} ions is prepared, a Zn^{2+}-phosphonic acid (PA) complex is formed in the solution.

(3) When the steel is immersed in this environment, the Zn^{2+}-PA complex diffuses from the bulk of the solution to the metal surface.

(4) On the surface of the metal, the Zn^{2+}-PA complex is converted into an Fe^{2+}-PA complex at the local anodic regions, because the iron complex is more stable than the zinc complex (Kuznetsov, 1990):

$$Zn^{2+} - PA + Fe^{2+} \rightarrow Fe^{2+} - PA + Zn^{2+}.$$

(5) The released Zn^{2+} can then form a $Zn(OH)_2$ precipitate at local cathodic regions:

$$Zn^{2+} + 2\ OH^- \rightarrow Zn(OH)_2 \downarrow.$$

(6) Thus the protective film consists of the Fe^{2+}-PA complex and $Zn(OH)_2$. This is the case with phosphonic acids such as HEDP, ATMP and 2-carboxyethyl phosphonic acid. In the case of phosphonic acids such as ethyl-2-chloroethyl and phenyl-phosphonic acids, the protective film also contains oxides of iron, in addition to Fe^{2+}-PA complex and $Zn(OH)_2$.

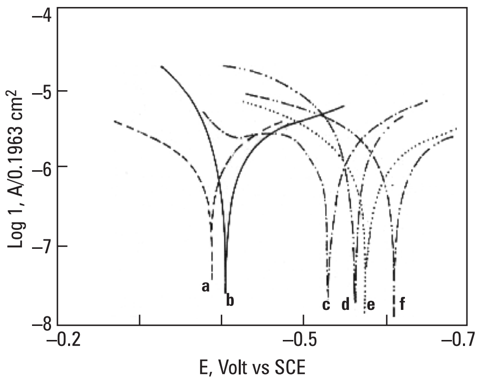
It is assumed in the above mechanism that the phosphonate functions as a transporter of Zn^{2+} from the bulk of the solution to the metal surface. In order to confirm this, the potentiostatic polarisation tests were carried out.

Potentiostatic polarisation studies

(I) The role of HEDP in the HEDP-Zn^{2+} system

The potentiostatic polarisation curves for carbon steel immersed in various environments are presented in Figure 1. When carbon steel was immersed in an aqueous environment containing 60ppm Cl^-, the corrosion potential was 389mV vs. SCE. When 100ppm Zn^{2+} was added to the above environment, the potential

Figure 1 Polarisation curves of carbon steel in various environments. (a) Neutral aqueous solution containing Cl^- 60ppm (blank); (b) Test solution plus Zn^{2+} 100ppm + HEDP 10ppm; (c) Test solution plus Zn^{2+} 100ppm + HEDP 50ppm; (d) Test solution plus Zn^{2+} 100ppm + HEDP 100ppm; (e) Test solution plus Zn^{2+} 100ppm + HEDP 200ppm; (f) Test solution plus Zn^{2+} 100ppm + HEDP 300ppm



shifted to a more negative potential (i.e. more cathodic) of –536mV vs SCE. This suggests that the predominant action of the Zn^{2+} ions is on the cathodic reaction. Steel immersed in solution containing 100ppm Zn^{2+} and 10 ppm HEDP had corrosion potential of –405mV vs SCE. When various concentrations of HEDP (50, 100, 200, 300ppm) were added to the environment, the corrosion potential shifted progressively to a more negative potential (i.e. more cathodic): –531, –563, –575 and –609mV vs SCE respectively.

This behaviour suggests that, as the concentration of phosphonic acid was increased, the amount of Zn^{2+} transported from the bulk of the solution to the metal surface also increased; the amount of $Zn(OH)_2$ deposited at cathodic sites also increased; and the cathodic reaction was more effectively prevented.

Thus, the polarisation tests revealed that phosphonates function as transporters of Zn^{2+} from the bulk of the solution on to the metal surface. The anodic reaction is controlled by the formation of Fe^{2+}-PA complex on the anodic sites, and the cathodic reaction is controlled by the formation of $Zn(OH)_2$ at cathodic sites.

Similar behaviour was observed for the systems containing 50ppm Zn^{2+} and various concentrations of HEDP, namely, 10, 50, 100, 200 and 300ppm. The corrosion potentials of steel immersed in these environments were –449, –528, –584, –597 and –632mV vs SCE respectively.

(II) The role of ATMP in the ATMP-Zn^{2+} system

The potentiostatic polarisation curves of carbon steel immersed in various environments are presented in Figure 2. When carbon steel was immersed in aqueous solution containing 100ppm Zn^{2+} and 10ppm ATMP, the corrosion potential was – 439mV vs SCE. When various concentrations of ATMP (50, 100, 200, 300ppm) were added to the environment, the corrosion potential progressively shifted to a more negative potential (i.e. became more cathodic): –446, –485, –500 and –546 mV vs SCE respectively.

This behaviour suggests that, as the concentration of the phosphonic acid was increased, the amount of Zn^{2+} transported from the bulk of the solution on to the metal surface also increased.

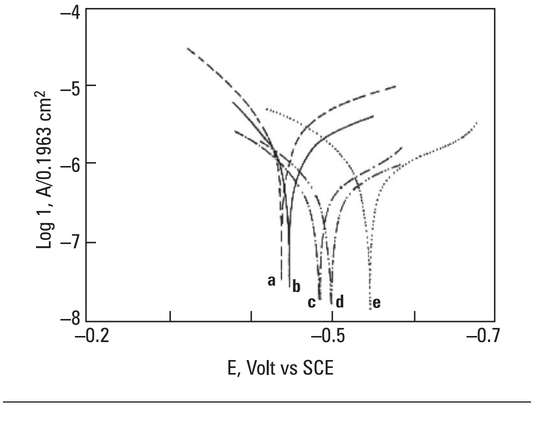
The polarisation tests indicated consistently that the phosphonates functioned as transporters of Zn^{2+} from the bulk of the solution to the metal surface, the anodic reaction was controlled by the formation of Fe^{2+}-PA complex, and the cathodic reaction was controlled by the formation of $Zn(OH)_2$ at cathodic sites.

Similar observations were made with carbon steel in solutions containing 50ppm Zn^{2+} and various concentrations of ATMP, namely 10, 50, 100, 200 and 300ppm. The corrosion potentials of the above systems were –373, –383, –430, –487 and –583mV vs SCE, respectively.

Weight loss study

The inhibition efficiencies offered to carbon steel by the various inhibitor systems, when

Figure 2 Polarisation curves of carbon steel in various environments. (a) Test solution plus Zn^{2+} 100ppm + ATMP 10ppm; (b) Test solution plus Zn^{2+} 100ppm + ATMP 50ppm; (c) Test solution plus Zn^{2+} 100ppm + ATMP 100ppm; (d) Test solution plus Zn^{2+} 100ppm + ATMP 200ppm; (e) Test solution plus Zn^{2+} 100ppm + ATMP 300ppm



immersed for a period of seven days in aqueous solution containing 60ppm Cl^-, are given in Table I.

It can be observed that, for a given concentration of Zn^{2+}, HEDP exhibited a higher inhibition efficiency than ATMP. For example, when the concentration of Zn^{2+} was 50ppm, HEDP showed 98 per cent inhibition even at a low concentration of 50ppm. However, ATMP at a 50ppm concentration had an inhibition efficiency of only 45 per cent. In order to achieve 98 per cent inhibitor efficiency, a relatively high concentration of ATMP (200ppm) was required. When the concentration of Zn^{2+} was increased, say from 50ppm to 100ppm, a still higher concentration of ATMP was required, but even 300ppm ATMP offered only 90 per cent inhibition efficiency.

The influence of phosphonic acid concentration on inhibition efficiency at a given Zn^{2+} ion concentration

It can be observed from Table I that, for a given concentration of Zn^{2+} ions, the inhibition efficiency increased, as the concentration of the phosphonic acid was increased. This is in agreement with the results of the polarisation studies, which indicated that, as the concentration of the phosphonic acid was increased, the transport of Zn^{2+} ions from the bulk of the solution on to the metal surface also increased, the extent to which controlling the cathodic reaction by deposition of $Zn(OH)_2$ precipitated at cathodic sites increased and, in consequence, the inhibition efficiency of the system increased. The concept was applicable to both the HEDP system and the ATMP system.

The influence of Zn^{2+} on the inhibition efficiency of phosphonic acid

It can be observed from Table I that, at higher phosphonic acid concentrations (100, 200, 300ppm), Zn^{2+} ions had no influence on the inhibition efficiency of the HEDP system. However, in the case of the ATMP system, the inhibition efficiency decreased, as the concentration of Zn^{2+} ions was increased (from 50ppm to 100ppm).

Table I Inhibition efficiencies (%) offered by various inhibitor systems to carbon steel immersed for a period of seven days in an aqueous environment containing 60ppm Cl^-

Phosphonic	Zn^{2+} (50ppm)		Zn^{2+} (100ppm)	
acid (ppm)	HEDP	ATMP	HEDP	ATMP
10	13	28	15	38
50	98	45	98	50
100	98	92	98	60
200	98	98	98	85
300	98	98	98	90

This observation can be explained by the fact, that at higher concentrations of Zn^{2+} ions, the Zn^{2+}-ATMP complex formed in the solution was stable (and insoluble), and was precipitated within the bulk of the solution itself. However, in the case of the HEDP system, even at higher concentrations of Zn^{2+} ions, the Zn^{2+}-HEDP complex remained soluble and in solution. Hence, the rate of transportation of Zn^{2+} ions to the metal surface was not retarded.

Comparison of the inhibition efficiencies of the HEDP-Zn^{2+} system and the ATMP-Zn^{2+} system

Analysis of results of weight loss tests, presented in Table I, reveals that, in the presence of Zn^{2+} ions, better inhibition efficiency was shown by HEDP than by ATMP. For example, the formulation consisting of 50ppm Zn^{2+} ions and 50ppm HEDP had an inhibition efficiency of 98 per cent, whereas the corresponding inhibition efficiency for the ATMP system was only 45 per cent. Similarly, with 100ppm Zn^{2+} ions in the test solution, a 98 per cent inhibition efficiency was exhibited in solution containing 50ppm HEDP, whereas the efficiency was only 50 per cent in the case of ATMP system. This was because, at a given concentration of Zn^{2+} ions, HEDP is a better transporter of Zn^{2+} than ATMP.

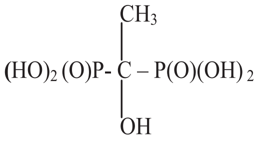
The conclusion was further supported by comparison of the corrosion potentials of carbon steel immersed in the 60ppm Cl^- environment in the presence of HEDP-Zn^{2+}, and the results from similar samples immersed in an environment inhibited by ATMP-Zn^{2+}. It is evident from Table II that, at a given concentration of Zn^{2+} ions, the shift in the corrosion potential of steel to a more cathodic value was greater in the case of HEDP than in that of ATMP. For example, in the presence of 50ppm Zn^{2+}, the addition of 300ppm HEDP shifted the corrosion potential to –632mV vs SCE, whereas the addition of 300ppm ATMP shifted the corrosion potential only to – 583mV vs SCE.

As per the details given in Table I, the corrosion inhibition efficiencies for carbon steel of the HEDP were consistently greater

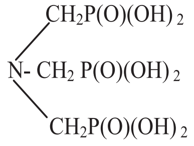
Table II Corrosion potentials (mV vs. SCE) of carbon steel immersed in the test solution containing various concentrations of inhibitor

Phosphonic acid (ppm)	Zn^{2+} (50ppm)		Zn^{2+} (100ppm)	
	HEDP	ATMP	HEDP	ATMP
10	– 449	– 373	– 405	– 439
50	– 528	– 383	– 531	– 446
100	– 584	– 430	– 563	– 485
200	– 597	– 487	– 575	– 500
300	– 632	– 583	– 609	– 546

than for ATMP in the test solution. This may be explained as follows:



HEDP



ATMP

ATMP is a triphosphonic acid, while HEDP is a diphosphonic acid. Additionally, the electron-releasing capability of ATMP is greater than that of HEDP. In consequence, the ATMP-Zn^{2+} complex is more stable in solution than the HEDP-Zn^{2+} complex. Therefore, when the HEDP-Zn^{2+} complex diffuses from solution to the metal surface, it splits easily into Zn^{2+} ions and HEDP. Zn^{2+} forms $Zn(OH)_2$ at the cathodic sites and HEDP forms the HEDP-Fe^{2+} complex at the anodic sites. Since the ATMP-Zn^{2+} complex is relatively more stable than the HEDP-Zn^{2+} complex (Chiesa *et al.*, 1985), it is not easily split into Zn^{2+} and ATMP, and hence the formation of $Zn(OH)_2$ and the ATMP-Fe^{2+} complex on the cathodic and anodic sites is not so easily facilitated.

It is the formation of both $Zn(OH)_2$ and the Fe^{2+}-phosphonate complex on the metal surface which is responsible for corrosion inhibition. Additionally, it is probable, though this was not confirmed, that the molecular size of the Fe^{2+}-HEDP complex is larger than the molecular size of the Fe^{2+}-ATMP complex, because of the difference in their structures (ATMP is relatively more packed). This factor could also help to explain the greater corrosion inhibition efficiency of HEDP than that of ATMP in the presence of Zn^{2+}.

Two factors influence the order of inhibition efficiency: (i) molecular size of the iron phosphonate complex, and (ii) the ease with which the phosphonate transports Zn^{2+} from the solution to the metal surface. If the size of the Fe^{2+}-ATMP complex is larger than the Fe^{2+}-HEDP complex, then the following explanation may be offered.

If the size of the iron phosphonate complex played the more dominant role, then the ATMP-Zn^{2+} system should have had better inhibition efficiency than the HEDP-Zn^{2+} system. However, the ATMP-Zn^{2+} system had a lower inhibition efficiency than the HEDP-Zn^{2+} system, and thus in this case the transporting ability of the phosphonate had a more dominant effect than the molecular size of the complex formed on the metal surface.

Conclusions

This study leads to the following conclusions:

- Phosphonates function as transporters of Zn^{2+} from the bulk of the solution towards the metal surface.
- The molecular size of the Fe^{2+}-phosphonate complex and Zn^{2+} transporting ability of the phosphonates influence the overall efficiency of corrosion inhibition.
- The "Zn^{2+}-transporting ability" of the phosphonates plays a more dominant role than the size of the Fe^{2+}-phosphonate complex.

References

Chiesa, W., Cigna, R., Di Simone, I.S., Gusmano, G. and Mazzani, G.F. (1985), *Proc. 6th Europ. Symp. Corrosion Inhibitors*, University of Ferrara, Italy, Vol. 2, p. 1295.

Dupart, M., Lafont, M.C. and Dabosi, F. (1985), *Electrochimica Acta*, Vol. 30 No. 3, p. 961.

Fang, J.L., Li, Y., Ye, X.R., Wang, Z.W. and Liu, Q. (1993), *Corrosion*, Vol. 49 No. 4, p. 266.

Felhosi, I., Keresztes, Zs., Karman, F.H., Mohai, M., Bertoti, I. and Kalman, E. (1999), *J. Electrochem. Soc.*, Vol. 146 No. 3, p. 961.

Gonzalez, Y., Lafont, M.C. and Pebere, N. (1996), *J. Applied Electrochem.*, Vol. 26, p. 1259.

Kuznetsov, Y.I. (1990), *Proc. 7th Europ. Symp. Corrosion Inhibitors*, University of Ferrara, Italy, Vol. 1, p. 1.

Rajendran, S., Apparao, B.V. and Palaniswamy, N. (2000), *Anti-Corrosion Methods and Materials*, Vol. 47 No. 2, p. 83.

Rodin, U.M., Podobaev, N.I. and Savitkin, N.I. (1987), *Zashch. Met.*, Vol. 23 No. 3, p. 491.

Sekine, I. and Hirakawa, Y. (1986), *Corrosion*, Vol. 42, p. 272.

Wranglen, G. (1985), *Introduction to Corrosion and Protection of Metals*, Chapman & Hall, London, p. 236.

Zanzucchi, P.J. and Thomas, J.H. III (1988), *J. Electrochem. Soc.*, Vol. 135 No. 6, p. 1370.

Zhu, C. and Zhou, W. (1989), *Hauzhong Shifan Daxuo Xuebao Ziran Kexueban*, Vol. 23 No. 4, p. 517.