Contributed papers

Inhibition by phosphonic acids – an overview

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Abstract

Phosphonic acids are good complexing agents. However, they are not good as inhibitors except for a very few. Synergistic inhibition is offered in the presence of metal cations like Ca^{2+}, Mg^{2+}, Zn^{2+} and others in neutral media. The zinc ion is an ideal choice. The part of zinc ions are now replaced by polymers, azoles to prepare eco-friendly inhibitor formulations. They are also used as corrosion inhibitors in concrete, coatings, rubber blends, acid cleaners, anti-freeze coolants, etc. Discusses the various applications of phosphonic acids and their action mechanisms.

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Introduction

Interphase inhibitors are effective for the decrease of metal corrosion in nearly neutral conditions by forming weakly soluble compounds with the metal ion existing in the solution which precipitates on to the surface to form a three-dimentional protective layer. Such inhibitors for cooling water treatment technology in the last decades comprise different types of phosphonic acids. Widely used examples of organic phosphonic acids are 1-hydroxy ethane-1,1-diphosphonic acid (HEDP)[1,2], aminotrimethylene phosphonic acid (ATMP), hydroxyphosphonoacetic acid (HPA), etc. Phosphonates are introduced alone or in combination with other metal cations. Research in this area has been stimulated by the need to develop inhibitor formulations that are free from chromates, nitrates, nitrites, inorganic phosphorus compounds, etc. Addition of phosphonic acids even with chromates[3] or nitrites[4] reduces the corrosion rate. Phosphonates contain phosphorous-carbon bonds (P-C) in inorganic phosphates. The P-C bonds are much more resistant to conversion into orthophosphate than the P-C bonds in inorganic phosphates.

Phosphonates when blended with certain metal cation and polymers reduce the optimal inhibitor concentration needed for inhibtion due to synergistic effects of components. Synergism is one of the important effects in the inhibition process and serves as the basis for all modern corrosion inhibitor formulations[5]. Pnodya[6] discussed the use of phosphonic acids especially HEDP and ATMP. While the acidic, complexing, adsorptive and anti-corrosive properties of aminophosphonic acids was discussed in another paper[7]. Kuznetzov *et al.*[8] discussed the influence of the chemical structure of phosphonic acid inhibitors and of the nature of complex formed on metal.

In this review, some of the easy preparations of phosphonic acids, the corrosive environment at which the phosphonic acids are tested for corrosion inhibition, the metal and alloy to be protected by phosphonic acids, inhibitor composition containing multi-component systems and other corrosion related application of phosphonic acids are presented.

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Preparation of phosphonic acids

Alkyl and aryl phosphonic acids

Haegele *et al.*[9] prepared 1-phenylethane-1,2,2-triphosphonic acid and its water soluble salts from chloro substituted styrenes. Thus 400ml of Na(O) $P(OEt)_2$ in THF was treated with 20g of $PhCCl = CCl_2$ and the other resultant product was hydrolysed to give 66 per cent 1-phenylethane-1,2,1-triphosphonic acid.

$$Na(O)P(OEt)_2 + PhCCl = CCl_2 \xrightarrow{THF} \text{Ester} \xrightarrow{\text{Hydrolysis}} \text{1-phenylethane-1,2,2-triphosphonic acid}$$

Issleib *et al.*[10] prepared methylphosphonic acid using $(Me_3SiO)_2PH$ and $(Me_3Si)_2NH$. Thus a mixture of $(Me_3SiO)_2PH$ 42g and $(Me_3Si)_2NH$ was mixed with freshly distilled acetyl chloride 7.8g in an argon atmosphere with temperature less than or equal to 70-80°C and cooled after mixing at this temperature for one hour, filtered and vacuum distilled. The yield is 72 per cent (38.4g).

Hydroxy substituted alkyl and aryl phosphonic acids

HDEP[11] was prepared by adding PCl_3 to an aqueous solution of acetic acid followed by heating to 100-115°C for one hour and cooling to 70°C.

$$PCl_3 + CH_3COOH \xrightarrow[2.\ 70°C]{1.\ 100-115°C,\ 1hr} HEDP.$$

Kalman *et al.*[12] prepared mono, di, and triphosphonic acids starting from phosphorus trichloride or phosphorus acid, e.g. a cooled mixture of 10.6g of benzene and 12g PCl_3 was treated with 30g of acetic acid to give after phase separation 71 per cent 1-hydroxyl-1-phenylmethane phosphonic acid.

$$C_6H_6 + PCl_3 + CH_3COOH \rightarrow C_6H_5CH(OH)PO_3H_2$$

Mikroyannidis[13] prepared hydroxy substituted mono and bisphosphonic acid from substituted phosphonates and trisphosphonates. Thus $P[(OH)_2(P(O)]_2C_6H_4$ was prepared from its substituted phosphonates by using acid hydrolysis.

Hydroxy, carboxy substituted alkyl or aryl phosphonic acids

$R\text{-}C(OH)\ (PO_3H_2)\ XCOOH$ (R = alkyl, alkenyl, cycloalkyl, aryl; X = alkylene, alkenylene and arylene) were prepared by Clubley *et al.*[14]. Thus 1 mole each of PCl_3 and ethylacetoacetate were heated at 50°C for 2.5 hours. Acetic acid (2 mole) was added and the mixture was heated at 70°C for three hours. Water was then added and refluxing continued for four hours to give 94 per cent 3-hydroxy-3-phosphonobutanoic acid.

Aminoalkyl or aryl phosphonic acids

Zhuang *et al.*[15] synthesized 1-aminoethylidine phosphonic acid ammonium salt using urea, acetic acid and PCl_3 with the yield of 40 per cent.

$$H_2N\text{-}C(O)\text{-}NH_2 + CH_3COOH + PC1_3 \rightarrow CH_3\text{-}CH(NH_2)\ (PO_3H_2)$$

1-aminophosponic acids are also prepared by using phosphonylation of nitriles[16]. Thus phosphonylation of RCN with phosphorus acid gave 37-85% $R\text{-}C(NH_2)\ [P(O)\ (OH)_2]_2$ (R = H, Me, Et, Ph, 4-pyridyl, etc.)

N-substituted 1-aminophosphonic acids

ATMP is prepared by refluxing ammonia, concentrated HCl, formaldehyde and phosphorus acid[17]. Redmore[18] prepared 1-aminophosphonic acid by direct addition of phosphorus acid to imines. Acetylaminoethane diphosphonic acid[19] was prepared by treating urea, acetic anhydride and methyl or ethylphosphite. Cook[20] prepared 28 parts of $HOOCCH(NEt_2)P(O)(OH)_2HClH_2O$ by refluxing diethylamine hydrochloride (16.3g), H_3PO_4 (16.6g) and 50 per cent glyoxalic acid 29.6 parts in five volume parts 80 per cent HCl for 18 hours.

Phosphonated amino acids

N-phosphonomethyl glycine[21] is prepared by refluxing one mole of glycone, two moles of phosphorus acid and four moles of formaldehyde in the presence of concentrated hydrochloric acid.

Cyclic phosphonic acids

Hwa *et al.*[22] prepared 4-phosphonomethyl 2-hydroxy-2-oxo-1,3,4-oxazaphosphoninane-N-oxide by using the following procedure. 2-aminoethanol in water in ice temperature was treated with phosphorus acid and then concentrated hydrochloric acid. The mixture was brought to reflux and aqueous formaldehyde was added to give after four hours, 4-phosphonomethyl-2-hydroxy-1,2,4-oxazophosphorinane. The latter in aqueous NaOH (pH10) was treated with 35.7 per cent hydrogen peroxide to give 4-phosphonomethyl-2-hydroxy-2-oxo-1,2,4-oxazaphosphoninane-N-oxide.

Phosphonic acids with multi-functional groups

Blun and Worms[23] prepared thiazenealkane phosphonic acid by cyclization of divinylsulphone with $H_2N\ (CH_2)n[P(O)(OH)_2]_2OH$ (n = 2.5,10) and Quinlan[24] prepared thiazenealkane phosphonic acid by cyclo-addition of $(CH_2 = CH_2)SO_2$ to an appropriate aminoalkane. Benzimidazodyl-2-alkane phosphonic acid[25] was prepared by O-phenylenediamine with $C_2H_5OOCCH_2CH_2P(O)(OC_2H_5)_2$. Thus 2.4 moles of O-phenylene diamine, 1,000g water, 1,000g HCl and 2.22 moles of $(EtO)_2P(O)CH_2CH_2COOC_2H_5$ was refluxed for 15-20 hours to give the above product. 2-phosphonomethylenethio-1,3-benzothiazole[26] was prepared by treating 2-mercaptobenzotriazole (MBT) with chloromethyl phosphonic acid.

Polyphosphonic acid

The poly (hydroxyphosphonic acids)[11,27] $R_1C(PO_3H_2)O[P(O)(OH)(R_1(PO_3H_2)O]nR$ (R = H, MeCO, HOOCCH = CHCO, $HOOC(CH_2)_2CO$; $C_6H_4(COOH)CO$; R_1 = saturated or unsaturated alkyl; n = 1-6) are prepared by reacting phosphorus acid with acetic with saturated and/or unsaturated aliphatic dicarboxylic acid anhydrides at 75-130°C. For example phosphorus trichloride was added to an aqueous solution of acetic acid followed by heating to 110-115°C for one hour and cooling to 70°C. The HEDP obtained was reacted with maleic anhydride at 100-115°C to give a polyhydroxy phosphonic acid.

Phosphonated hydrolytic polymaleic anhydride[28] is prepared in a one step process by using hydrolytic polymaleic anhydride and phosphorus acid.

Polyphosphono carboxylic acid

Phosphono (carboxylic acid)[29] is prepared from dimethyl phosphite, methylacrylate, dimethyl maleate telomer of the form (OH) PO $(CH_2CRCOOH)$ n (CHCOOHCH-COOH) mH where R = H, CH_3; n and m = 1-49 (but n + m is less than or equal to 50).

Polyvinyl phosphonomethylaminocarboxylates

Polyvinyl phosphonomethylaminocarboxylates[30] were prepared by the following method. Poly(vinylpyrollidone) (MW = 10,000) 70g, phosphorus acid (49.9%) 82g, hydrochloric acid (37%) 57g was refluxed for two hours, 18g of paraformaldehyde was added over one hour and the solution refluxed for 24 hours to give a product with a degree of phosphonomethylation of 0.166.

Phosphonated polyamides

Polyamides containing phosphonic acid and N-methylene phosphonic acid groups were prepared by treating polycaprolactum with formaldehyde and PCl_3 in a non-aqueous medium[31]. NMR spectra of these compounds confirmed that the acid groups are bonded to both nitrogen and carbonyl atoms of the polyamides.

Corrosion inhibition studies

Corrosive environment

Chloride

Various concentrations of chlorides are used for the testing of corrosion inhibition of phosphonic acids. Concentration of chloride used depends on the purpose of the study. Gunasekaran *et al.*[32,33] used 60ppm of chloride for the testing of 2-carboxyethyl phosphonic acid (2CEPA). Kuznetzov *et al.*[34] used 0.01M NaCl for the testing of iminocarboxy phosphonic acids and HEDP and Sekine *et al.*[35] used 0.3 per cent NaCl for HEDP efficiency of most of the phosphonic acids[36-40]. Sodium chloride was taken as the chloride source in most of the experiments. Sometimes calcium chloride and potassium chloride have also been used[34]. Sodium perchlorate 0.5M/L is also used as a corrosive medium for examining the corrosion inhibition efficiency of phosphonates (HEDP)[41].

Sulphates

Sulphates were used in the range of 200mg/L to 0.5 M/L for the testing of phosphonate inhibitors[42-49]. Sulphate 200 mg/L was used by Kuznetzov *et al.*[47] for testing the corrosion inhibition efficiency of NTMP and Kubicki *et al.*[44] used 1.5 M/m^3 sulphate solution for ATMP. The source of sulphate is sodium sulphate and sometimes potassium sulphate[43].

Carbonates

Water hardness is mainly due to calcium and magnesium carbonates. The performance of phosphonates as corrosion inhibitors is also tested in the presence of carbonates of calcium, magnesium, potassium and sodium. The corrosion inhibition efficiency of HEDP is tested[50] using 300ppm of total hardness ($CaCO_3$ and $MgCO_3$) but Kuznetzov *et al.*[51] used equal or less than 10mg equiv/L calcium hardness for HEDP. Boffardi[52] used 318mg/L calcium carbonate to study the corrosion inhibition efficiency of ATMP. Vanloyen *et al.*[53] used different carbonate hardness to check the corrosion inhibition efficiency of HEDP. Sodium bicarbonate and potassium carbonate were also used to identify the corrosion inhibition efficiency of phosphonic acids[44,46,54].

pH

pH is a crucial factor for the determination of corrosion inhibition efficiency of phosphonic acids. Most of the phosphonic acids are pH selective. The nature of pH selectivity of phosphonic acids depends on the metal, the composition of inhibitor, etc. Nitrogen containing phosphonic acids are effective at decreaseed pH (acidic levels). Thomas *et al.*[55] used a composition containing ATMP at pH 1-4; Kruchenko and Sabirova[36] used NTMP at pH5. Zhou *et al.*[42] used ATMP in 0.10m/l sulphuric acid. Notoya *et al.*[56] used bis[(benzotriazolyl) methyl] phosphonic acid in acid medium. Horvath and Kalman[57] used diethylenetriaminepentaphosphonic acid in acid solutions. Some of the phosphonic acids not having a nitrogen group were also tested in low pH, e.g. 1,6-hexane diphosphonic acid[42], and HEDP[38]. The HEDP zinc ion combination even works at alkaline pH[38].

Temperature

Temperature depends on the use of phosphonic acids for the systems like cooling water, boiler, etc.[34,54,58-60]. The maximum temperature is 60°C for cooling water plants. Kuznetzov *et al.*[60] used HEDP at elevated temperature for studying the corrosion inhibition efficiency and Kruchenko and Sabirova[36] used NTMP at 363K. He[54] and Wang[58] prepared inhibitor composition containing ATMP or ATMP with HEDP for boilers.

Metals and alloys

Iron

Phosphonic acids have been used frequently to protect iron and its carbon alloys (see Table I) in natural medium. HEDP is the phosphonic acid which is widely used to protect iron and its carbon alloys. Kuznetzov *et al.* studied the corrosion inhibition of mild steel using HEDP in combination with zinc ions[61,62]. The other phosphonic acids which are frequently used for the corrosion inhibition of iron and its carbon alloys are aminotrimethylenephosphonic acid (ATMP), nitrilotrimethylene phosphonic acid (NTMP), 2-phosphonobutane 1,2,4-tricarboxylic acid (PBTC) and hydroxyphosphonoactic acid (HPA). Other phosphonic acid such as 1,6-hexanediphosphonic acid (HEP), phenylenebis phosphonic acid, ethylenediaminetetramethylenephosphonic acid, diethylenetriamine pentamethylenephosphonic acid, methylphosphonic difluoride, N-phosphonomethylglycine, disodium dodecylphosphonate and disodium monoalkylphosphonate are also used for the corrosion inhibition of iron and its carbon alloys.

Stainless steel

Very few references are available in the literature regarding the corrosion inhibition of

Table I List of metals and the phosphonic acids studied

Metals and alloys	Phosphonic acids
Iron	HEDP
	ATMP
	NTMP
	PBTC
	HPA
	1,6-hexane diphosphonic acid
	1,4-phenylene bis phosphonic acid
	Ethylene diamine tetramethylene phosphonic acid
	Methyl phosphonic difluoride
	N-phosphono methylglycine
	Diethylene triamine pentaphosphonic acid
	Disodium dodecyl phosphonate
	Disodium monoalkyl phosphonate
	Ortho hydroxy benzene phosphonic acid
Stainless steel	HEDP
	ATMP
	NTMP
	Methyl aminodimethylene phosphonic acid
	n-butyl aminodimethylene phosphonic acid
	Methylphosphonodifluoride
Aluminium	HEDP

stainless seel using phosphonic acids. Bartonicek *et al.*[63] used NTMP for the protection of chromium nickel steel and Sekine *et al.* used HEDP to protect SS-304 stainless steels. Zhou *et al.*[64] used various phosphonic acids such as ATMP, methylaminodimethylenephosphonic acid, n-butylaminodimethylenephosphonic acid and HEDP for the corrosion inhibition of Cr-13 stainless steels in acid medium. Zabielski *et al.*[65] used methylphosphonic difluoride for the corrosion inhibition of 316L stainless steel and 304 stainless steel.

Aluminium

Next to iron and its carbon alloys, aluminium and its alloys are protected by phosphonic acids in cooling water systems. Nitrogen containing phosphonic acids, especially NTMP, are used for the corrosion inhibition of aluminium and its alloys[63,66-68]. Kuznetzov *et al.*[69] used HEDP for the protection of aluminium and its alloys. The other phosphonic acids which are used for the corrosion protection of aluminium and its alloys are aminomethylene phosphonic acid (AMP), iminocarboxyphosphonic acids, ATMP and gem-diphosphonates.

Copper

Nitrogen-containing phosphonic acids are mostly preferred for the corrosion inhibition of copper. The exception is HEDP[70]. NTMP has been used by Bartonicek *et al.*[63] and Falewicz *et al.*[66] for the corrosion inhibition of copper. Sherwood *et al.*[71] used 2-acrylamido-2-methylpropyl phosphonic acid and 2-methylacrylamido-2-methylpropyl phosphonic acid for the corrosion inhibition of copper. Yamada *et al.*[72] used an ATMP benzotriazole mixture and Notoya *et al.*[56] used bis[(1-benzotriazolyl) methyl] phosphonic acid for the corrosion inhibition of copper. Zhu *et al.*[26] used a phosphonic acid with a thiogroup such as 2-phosphonomethylenethio-1, 3-benzotriazole (PMPB) for the corrosion inhibition of copper.

Brass

The use of phosphonic acid in corrosion inhibition of brass is lower in comparison with the use of phosphonic acids for corrosion inhibition of copper. Very few examples are available in the literature for the corrosion inhibition of brass using phosphonic acid [4,48,63,66,70]. Vanloyen[70] used HEDP for the corrosion inhibition of brass. Batonicek *et al.*[63] and Falewicz *et al.*[66] used NTMP for the corrosion inhibition of brass.

Other metals and alloys

Phosphonic acids such as NTMP and HEDP were used for the corrosion inhibition of some of the copper alloys such as $CuZn_{20}Z_{12}$[70], $AlCu_4Mg_1$[66] and $CuNi_{10}Fe_1Mn$[72]. In the case of corrosion inhibition of magnesium[65] and its alloy Mg_2Al[63] methyl phosphonic difluoride and NTMP were used.

Inhibitor composition and its effect on corrosion rates

Phosphonic acid alone

HEDP. Wang *et al.*[73] used 12ppm of HEDP and chlorine as algicide and bactericide in circulating cooling water in a plant for C_4 extraction (SiC) and butadiene manufacturing plant. The corrosion rates of test periods of 33, 49 and 52 days were 0.039mm/yr, 0.049mm/yr and 0.056mm/yr respectively. Scaling rates for test periods of 52, 69 and 72 days were 40.8mg/cm^2, 39mg/cm^2 and 11.76mg/cm^2, respectively.

Impedance spectra of carbon steel in the presence of HEDP was studied in neutral solutions by Kalman *et al.*[74]. Results of these studies show that at low concentration HEDP inhibits carbon steel corrosion by a precipitative mechanism by forming insoluble iron complexes and repairing the porous oxide layer formed on the metal surface. Increasing the HEDP concentration beyond the optimal value decreases its corrosion inhibition efficiency due to the dissolution of the oxide layer. Zocher[75] also studied the corrosion inhibition of HEDP and its sodium salt.

NTMP. Venables[67] studied the corrosion rate of aluminium and steel surfaces in the presence of NTMP. He found that NTMP inhibits both aluminium and steel. Zanucchi *et al.*[68] treated aluminium with NTMP and examined the surface with infrared spectroscopy and X-ray photoelectron spectroscopy. These measurements show NTMP reacts with the aluminium surface to form a coating which is an effective inhibitor.

1,1-Di(1-phosphonopropionic acid). 1,1-di (1-phosphonopropionic acid) and its sodium salts shows excellent corrosion inhibition and scale prevention in stabilization of water[76].

N-methylaminophosphonic acid. Pyrwanow *et al.*[77] studied the sorptive properties and thermodynamic properties of adsorption of ethylenediaminetetraphosphonic and n-octaminedimethylenephosphonic acid on a solid iron electrode in a neutral medium using electrical double layer differential capacitance. The inhibiting properties of components were determined using the gravimetric method. The corrosion inhibiting properties of phosphonic acid were due to localized chemisorption on the metal surface.

Alkylphosphonic acids. Using the current-potential curves of pure iron in 0.5 M sodium sulphate as a standard, the corrosion inhibition effect of 1,4 phenylenebis-phosphonic acid on corrosion of iron was investigated by Erbil[45] with a rotating disc system under oxygen and hydrogen atmosphere. Current potential curves in 1.0.5M sodium sulphate with and without the inhibitor and kinetic results showed that within $4 < pH < 5$, 1,4-phenylenebisphosphonic acid is a weak surface active inhibitor under hydrogen atmosphere.

Isopropenyl phosphonic acid copolymers were used by Becker[77] for the corrosion inhibition of steel and they act as effective inhibitors and anti-scalants. The influence of disodium monoalkyl phosphonates $R(PO_3H_2)_2$ ($R = C_4H_9$, C_5H_{11}, C_6H_{13}, C_7H_{15}, C_8H_{17}, $C_{10}H_{21}$) on the corrosion rate of steel type Xc38 was examined by voltametric and impedance techniques[40]. The formation of a relatively compact adherent film of disodium monoalkylphosphonates caused a decrease in the corrosion rate.

Phosphonic acid metal ion mixture

With very few exceptions, most of the phosphonic acids as such are not good corrosion inhibitors. Their corrosion inhibition properties were increased by the addition of metallic ions. These metallic ions form insoluble complexes with phosphonic acids and repair the porous oxide layer and prevent further corrosion. Predominantly zinc ions are used for elevating the corrosion inhibiting properties of phosphonic acids. The zinc phosphonate complexes give very good corrosion inhibition. Metallic cations for using in phosphonate inhibitor mixtures are Ca^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Mn^{2+}, Sn^{2+}, Cu^{2+}, Ba^{2+}, Sr^{2+}, Al^{3+}, Cr^{3+}, etc.

Phosphonic acid with zinc ion. Corrosion inhibition efficiency of HEDP and zinc ion mixture was elaborately studied by many authors. The effect of HEDP on the corrosion rate of copper, brass and other copper alloys in cooling water were studied gravimetrically by using a recirculating loop of Vanloyen[70]. HEDP decreases the corrosion rate of copper and its alloys in the presence of zinc ions.

Terekhim *et al.*[50] studied the effect of HEDP and zinc ions on the corrosion rate of steel ST-3 with varying hardness and temperature. Radioactive tracers and potentiometry were used to determine the effect of zinc ion concentration on the adsorption of HEDP on a low alloy steel and its corrosion inhibition efficiency by Konya *et al.*[41]. The HEDP concentration (0.0003-0.005 M/L) adsorption on steel in 0.5M/L sodium perchlorate solution attained a maximum at zinc ion/HEDP ratio 2.

Kuznetzov *et al.*[51,78,79] studied the protection of low carbon steel from corrosion by HEDP and its composition with zinc sulphate in the presence of calcium and magnesium salts as well as stability of solutions at pH 5.7–8.3. The introduction of HEDP and zinc ions improves the protection of steel from corrosion. The use of zinc ion, HEDP complexes are more effective in water with calcium hardness less than or equal to 10mg equiv/L in harder water for stabilizing the solutions; their pH must additionally be controlled. The corrosion rates of steel in the presence of supporting electrolyte sodium chloride 30mg/L and sodium sulphate 70mg/L were also determined using weight loss.

Hydroxyphosphono acetic acid (HPA) with zinc ion is a suitable ferrous alloy corrosion inhibitor for cooling towers that is non-toxic to aquatic life and decomposes to simple compounds. The testing sequence included aerated solution bottle tests (corrosion rate 0.3mm/yr), recirculating water rig tests alone and with additives, pilot cooling water rig tests and a field trial. HPA was compatible in formulations containing polymers for scale control, non-ferrous metal inhibitors, biocides for sludge control and zinc ion for soft water conditions.

In aqueous cooling and heating systems, scale formation and corrosion are prevented by addition of an organophosphonic acid such as ATMP with zinc ion. Dricker *et al.*[80] used the mixture of $Zn_3N(CH_2PO_3)_3$ 10-40 wt% and $Zn_5[N(CH_2PO_3)]_2$ 60-90 wt%. Kuznetzov *et al.*[34] used the electrochemical and weight loss method to study the pitting action of complexes in aqueous solution of chlorides for aluminium. The effect of inhibitors increases during the use of iminophosphonates in a composition with cation-complexing agents in particular with zinc ion. Depending on the hydrodynamic conditions,the temperature and the solution pH, as well as the composition of zinc phosphonates, they are capable of slowing down the occurrence of both electrochemical reactions, among them the cathodic reduction of oxygen.The studies were made in borate buffer solution, primarily at pH 7.36 containing 0.1M NaCl as well as aqueous solution of KCl and calcium chloride at different concentrations.

Kalman *et al.*[81] prepared N-phosphonoaminocarboxylic acids from amino acids. They studied the corrosion inhibition efficiency of these phosphonic acids with and without zinc ion using impedance spectroscopy, weight loss and potentiostatic polarization in order to show the significance of $CH_2PO_3H_2$ substitution.

Phosphonic acids with other metal ions

The metal ions other than zinc ion such as Ca^{++}, Mg^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Mn^{2+}, Sn^{2+}, Cu^{2+}, Fe^{2+}, Ba^{2+}, Sr^{2+}, Al^{3+},Cr^{3+} and metavanadate ion are also used with phosphonic acid to increase the corrosion inhibition efficiency of phosphonic acids. Usually zinc ions are hazardous to the environment. Zinc was converted to zinc sulphide by sulphate reducing bacteria. This zinc sulphide is cathodic to mild steel resulting in localized corrosion. Some of the authors tried to eliminate zinc from phosphonic acid inhibitor mixture by substituting environmentally friendly metal ions. The replacement and widely used other metal cation is calcium ion. Much of the study on calcium ion adsorption has been done by Kalman *et al.*[81-84]. They used various corrosive media and studied adsorption of HDEP and calcium ion on the surface of steel. Potentiometry and radioactive tracers[41] were used to determine the effect of calcium ion concentration on the adsorption of HEDP on a low-alloy steel and on its corrosion inhibition efficiencies in the presence of 0.5 mole/L of sodium perchlorate. The adsorption of HEDP increases with increase of Ca:HEDP mole ratio.

X-ray induced photoelectron spectroscopy, Auger spectroscopy and radioisotopes were used by Kalman *et al.*[82] for the identification of the effect of calcium ion on the adsorption of HEDP at steel surface. Calcium ions also used with ethylenediaminetetramethylene phosphonic acid and its corrosion rates were determined[85]. Kuznetzov *et al.*[8,79,86,87] discussed the effect of various metal ions such Mg^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Mn^{2+}, Sn^{2+}, Cu^{2+}, Ba^{2+}, Sr^{2+} and Al^{3+} on phosphonate complexing agents. They have also used divalent metal ions and rare earth metal ions such as ceriam on NTMP. Terekhin *et al.*[50] and Rodin *et al.*[43] used Fe^{2+}, Co^{2+}, Mg^{2+}, Zn^{2+}, Al^{3+}, and Cr^{3+} on HEDP and studied the effect of this inhibitor mixture on corrosion inhibition efficiencies.

Multi-component inhibitor mixture with metal cation

The addition of organic and inorganic compounds to inhibitor mixture, not only increases the corrosion inhibition efficiency of the inhibitor mixture but also reduces the requirement of phosphonic acids and metal cations. Thus addition of organic and inorganic compounds to inhibitor mixture reduces the cost of the inhibitor system markedly and reduces the pollution of water.

Phosphonic acid metal cation and organic compounds

The effect of corrosion inhibitor sodium salt of HEDP with and without additon of zinc ion and sodium gluconate on the corrosion inhibition of unalloyed steel (0.20, 0.08P and 0.06%S) in cooling water with different carbonate hardness was studied by Vanloyen *et al.*[53,88] using a recirculating loop. The optimal inhibition is attained by using sodium salt of HEDP, zinc ion and sodium gluconate.

The NTMP, phthalic acid anhydride and zinc sulphate as a three component has good adsorption and corrosion inhibition properties. The corrosion inhibition rate of steel even of multination systems is over 90 per cent for this solution. Kubicki *et al.*[44] did statistical optimization of the following corrosion inhibitor composition ATMP, phthalic acid anhydride and zinc sulphate for the protection of steel in water containing calcium chloride (3 moles/m^3), sodium sulphate (1.5 moles/m^3) and sodium carbonate (0.16 moles/m^3). The optimal inhibitor composition was ATMP 45g/m^3, phthalic acid anhydride 8g/m^3 and zinc ion 8g/m^3. The corrosion inhibition efficiency is 98 per cent.

Falezics *et al.*[66] studied the inhibitor mixture which contains NTMP, oxalic acid or phthalic acid anhydride and zinc sulphate.

Using gravimetric techniques, the influence of this mixture on the rate of corrosion of steel ST38 in stimulated industrial water of variable chemical composition and in water being chlorinated was studied. The influence of this mixture on the rate of corrosion of copper, brass, zinc and aluminium alloy was studied and a considerable decrease of the corrosion rate by the inhibitor mixture has been established. NTMP is combination with phthalic acid anhydride and zinc ion can therefore be considered as a prospective inhibitor for the corrosion protection of industrial cooling and heating water installations. 2-carboxyethyl phosphonic acid (2CEPA) together with zinc ion and calcium gluconate was studied by Gunasekaran *et al.*[33] for the corrosion inhibition of mild steel. Addition of calcium gluconate reduces the requirement of 2CEPA and zinc ion to half.

Phosphonic acid, metal cation with organic and inorganic compounds. The corrosion and electrochemical behaviour were studied of ST3 and Armco iron in neutral media (temperature in the range of 20°C to 90°C) in the presence of HEDP, zinc ion, the disodium salt of EDTA, sodium nitrite and benzoic acid by Kuznetzov *et al.*[60]. The inhibition of steel corrosion by the complex-ion is a consequence of the simultaneous formation of insoluble complex-ions on its surface and alkylation of the near electrode layer depending on the nature of the oxidizing agent and the solution temperature.

Wang *et al.*[58] used an alkyl composition as corrosion inhibitor in a recirculating water system which comprises the sodium salt of HEDP (5-15 wt%), sodium salt of ATMP (5-15 wt%), polysodium potassium silicate (20-40 wt%), water soluble sodium humate (5-25 wt%) and zinc carbonate (1-5 wt%). The composition is suitable for use in boilers for scale control.

The composition for preventing corrosion and scale in aqueous recirculation system comprises an aqueous solution with pH 2-13.5 containing 2-phosphonobutane – 1,2,4-tricarboxylic acid (PBTC) or its water soluble salts, a water soluble zinc complex with 1:(3.2) wt ratio with zinc ion polymer species and a water soluble orthophosphate at weight ratio with zinc ion of 1.5:1. The polymer is terpolymer comprising acrylic acid, methacrylic acid and N-alkylated acrylamide monomer having molecular weight 2,500-25,000. Additionally the composition may contain components such as tolytriazole, polyphosphates, phosphonic acids and acrylic polymers. Thus one effective composition for cooling water systems containing mild steel and hard water was zinc ion 1ppm, orthophosphate 4ppm, PBTC 2ppm, tolytriazole 2ppm and acrylic acid methacrylic acid-N-t-butylacrylamide copolymer 7.5ppm (water basis).

In a system with stimulated recycling conditions, decarbonated well water with relatively high calcium hardness (calcium content = 146mg/L pH 7.00), chloride 134mg/L, sulphate 99mg/L and conductance 650 micro s/cm was concentrated to one-third of its volume in two days and held for 12 days in a constant condition. The inhibitor added contains diethylenetriamine pentamethylene phosphonic acid, ethanolamine phosphate, anionic polymeric dispersants, azole components, zinc salts, chromates, phosphates, etc. After 14 days the calcium concentration was 398mg/L and coupon corrosion inhibition was 86.1 per cent.

Metal-free inhibitor composition. Very few literature examples are available for metal-free composition for corrosion inhibition. The most widely used phosphonic acid for metal free composition is HPOA[87]. Mitchel[89] prepared a metal-free composition by using HPA and the copolymer formed from 2-acrylamide-2-methylpropanesulphonic acid and acrylic acid and methacrylic acid. The respective corrosion rates of steel coupons in the recirculating line and in the tank in the test solution containing the inhibitor composition is 11.7mils/yr vs 30.8 and 34.3mils/yr for the coupons in the test solution containing no inhibitor. Hwa *et al.*[90] prepared an inhibitive formulation using HEDP, HPA and an azole compound. The corrosion inhibitor in water preferentially 5-200 pm of HEDP and HPA and 0.4-50ppm of azole compound. The water is suitable for heat exchangers and cooling water systems. SAE1010 steel coupons were immersed for three days in hard water at 130°F and pH 8-8.5 and flow rate 2ft/s. The corrosion rate was 5.6 mils/yr with the inhibitor, 5ppm of each HEDP, HPA and 1.94 ppm of sodium tolytriazole and 8.1 mils/yr at 10ppm HPA and 1.94 ppm of sodium tolytriazole and 87.5 mils/yr without the inhibitor.

Ciba[91] prepared corrosion inhibitor composition with HPA together with acrylic acid-lower alkylhydroxy acrylate polymers or sulphonated styrene maleic acid anhydride coploymers of sulphonated styrene copolymers or combined, which was effective against metal corrosion and scale deposition. Dabosi *et al.*[92] used polyaminopropyleneamine with ATMP as corrosion inhibitor for carbon steel in 3 per cent solution. Maleic acid anhydride polymer and ATMP combination is used by Boffari[52] as corrosion inhibitor for steel 1010. The steel 1010 specimens were suspended in water at 50°C, pH 7, total hardness $CaCO_3$ 318mg/l, corrosion rate was 4.2-4.6mils/yr. Poly (acrylic acid) 8ppm, benzotriazole 1ppm, high molecular weight sulphonated polystyrene 1ppm and hexamethylene diaminetetramethylene phosphonic acid 0.93ppm mixture was used as corrosion inhibitor by Lipinski[93]. The corrosion inhibition of the above mixture is 94 per cent compared with 81.7 per cent for a composition that does contain the phosphonic acid derivative.

Microemulsion

The corrosion inhibition of microemulsion composed of disodium 1-dodecanamido-1-methylethyl phosphonate ($DAMEPNa_2$)-heptane-pentanol-tapwater was studied by Zhu *et al.*[94] using the weight-loss method, polarization curves and an electron microscope. The results showed that $DAMEFNa_2$ in the microemulsion has an excellent inhibition effect. The efficiency of corrosion inhibition was above 90 per cent but it was only 16.2 per cent in the non-micro emulsion system.

Other applications related to corrosion inhibition

Concrete

Corrosion of steel reinforcement members in concrete is inhibited by adding phosphonic acid to the slurry. Alternatively an existing concrete structure is repaired by pouring a concrete slurry containing the corrosion inhibitor on the top and allowing it to migrate through the structure and contact the reinforcing members. Neagle *et al.*[95] studied the polarization resistance of EN33 mild steel electrodes in a simulated chloride solution containing 100ppm of HPA. The resistance was 4,300 kilo ohms cm^2 after immersion for 12-25 days in inhibitor solution compared to only 12.1kilo ohms cm^2 for the specimens exposed to the solution not containing the corrosion inhibitor. Mirita *et al.*[96] added HEDP-Zn salt to reinforced mortar which effectively prevented rust formation of steel bars.

Coatings

Matienzo *et al.*[97] used phosphonic acid and silanes to improve the durability of adhesion between aluminium and polymeric coatings. Of the silanes and phosphonates tested, NTMP is the among more effective corrosion inhibitors for the prevention of environmental degradation and improvements of adhesion between etched aluminium alloy substrates and epoxy coatings (a nitrile modified epoxy adhesive and an epoxy-polyamide top coat) as determined by the wedge test. Dofman *et al.*[98] studied the corrosiveness of modified polyethylene in metal polymer structures. Corrosion steel coated with low density polyethylene containing 3-22 per cent of fireproofing agent, poly (vinyl methylphosphonate) prepared from polyvinylalcohol and methyl phosphonic acid (1.0:1.3 and 1:1 ratio) completely eliminated the possibility of atmospheric moisture getting on steel fire proofed polymer interface.

Rubber compounds

Labacheva *et al.*[99] used flouro rubber acrylonitrile grafted EPDM rubber blends for improved corrosion and ozone resistance. It is prepared by addition of 1-30 parts of unsaturated (i.e. dehydrochlorinated) chlorinated polyethylene (25-30 per cent Cl) and 1-30 parts bis (1-acryloylogxy-3chloro-2-propanol) methyl phosphonate to mixtures of $F_2C = CF(CF_3)$-$F_2C = CF_2$ copolymer 10-75 per cent, EPDm rubber (containing 15-29 per cent grafted acrylonitrile 25-90 per cent, ZnO 5-10 per cent, MgO 5-10 per cent, 1,1-di (tert-butylperoxyl)-1,4-diisopropylbenzene 4-10 per cent and carbon black 30-80 per cent. Niess *et al.*[100] also prepared rubber compounds for metal surfaces using (2-chlorovinyl) phosphonate.

Combined cathodic and inhibitive protection of steel

Kuznetzov *et al.*[101,102] used combined protection of steel in sea water by phosphonate inhibitor and cathodic polarization. The cathodic polarization sharply decreases the corrosion rate of steel in sea water with the use of 10mg/l $Na_2H_2PO_4$ and HEDP. A synergistic effect of Zn-HEDP is observed. The protective cathodic film on the steel consists of

Mg (predominant), P and Zn. The combined protection method is useful for ballast compartments of ships.

Anti-corrosive water thinned inks for ball-point pens

The anti-corrosive water thinned inks for ballpoint pens was prepared by Suzuki[103] by using a mixture of C.I. acid red 8.75 per cent, ethylene glycol 15.0 per cent, glycerin 10 per cent, polyoxynonyl phenyl ether 0.3 per cent, ATMP 0.1 per cent, phenol 0.1 per cent and water 69.5 per cent. The ball-point pen filled with the above ink wrote smoothly initially and after one month storage at 50°C and produced no rust when kept in partial contact with a steel bar at 40°C for ten days while a control without ATMP wrote scratchily after the storage and produced rust on steel.

Bonnke *et al.*[104] used [(hydroxy phenyl)alkyl] phosphonate as corrosion inhibitor for polyolefin moulding compositions. Paladini used hydroxydiphosphonic acid derivatives of caprylic, lauric, palmitic, stearic, undecenoic, oleic or hexane carboxylic acids for the preservation of organic products. Thus a steel rod of 8.4cm^2 was immersed in a test tube filled with 6g of fatty acids and containing laurylhydroxy diphosphonic acids as inhibitor. After 36 hours, the Fe content in fatty acids was 21.1ppm or 12.05ppm when the inhibitor concentration was 800ppm or 1,600ppm, compared with 104.4ppm when no inhibitor was added. Boron *et al.*[105] used 50g/m^3 ATMP, 150g/m^3 sodium phosphate mixture for controlling corrosion of steel in steel spray cooler. French *et al.*[106] used PBTC for corrosion inhibition in coal slurries. Wilson[107] used disodiumethylphosphonate (0.002-0.006 wt %) and sodium mercaptobenzortriazole (0.2-0.3 wt %) for the effective corrosion inhibition for high pH solders in aqueous alcohol containing anti-freeze systems for internal combustion engine raditors. Hirozawa *et al.*[108] prepared corrosion inhibitors for anti-freeze coolants using 1-hydroxy-1, 1-diphosphonic acid. Cook[109] used hydroxy, carboxy phosphonic acids as fouling agents in aqueous systems. Hydroxycyanomethyl phosphonic acid[110] is used a corrosion inhibitor for preventing tartar and stabilizing tooth enamel.

Summary

In general phosphonic acids are very good complexing agents. Many of the phosphonic acids including polymeric phosphonic acids are easily prepared in laboratory conditions. The corrosion inhibition efficiency of phosphonic acids are tested using various conditions such as chloride, sulphate, hardness (calcium and magnesium hardness), pH, temperature, etc. Usually phosphonic acids are, as such, not good corrosion inhibitors. But the corrosion inhibition is increased by addition of metal cations especially zinc. The other metal cations used for the above purpose are Ca^{2+}, Mg^{2+}, Sn^{2+}, Co^{2+}, Cr^{3+}, Al^{3+}, Ni^{2+}, Fe^{2+}, etc. But zinc ion is the ideal metal cation for the combination with any phosphonic acids. The problem with the zinc ion is the formation of zinc sulphide by sulphate reducing bacteria and its toxicity. The amount of zinc ion and phosphonic acid required for corrosion inhibition is reduced by addition of organic compounds such as oxalic acid, phthalic acid anhydride, gluconate, etc. and inorganic compounds such as phosphates, etc. Some authors tried to eliminate the metal cation by addition of polymers, azole compounds with phosphonic acids. The most widely used compounds for this purpose are acrylic and are frequently used for the protection of iron and its alloys. The phosphonic acids are not only used as corrosion inhibitors in cooling water systems, but they are also used in boilers. Phosphonic acids are also used as corrosion inhibitors in concrete, coatings, rubber blends, acid cleaners, antifreeze coolants, ship ballast compartments, preservation or organic products, coal slurries, etc. The above applications show that phosphonic acids have an excellent role in corrosion inhibition compared to that of any other compounds.

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