



A CRITICAL REVIEW OF CORROSION INHIBITION BY PHOSPHONIC ACIDS

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Phosphonic acids are effective chelating agents. They bind strongly to metal ions. Phosphonic acids have also been widely used as corrosion inhibitors along with various metal ions as Zn^{2+} . The corrosion of various metals such as mild steel, copper, and aluminium have been prevented by phosphonic acids. Phosphonic acids exhibit good corrosion inhibition efficiency in acid medium, alkaline medium, and neutral medium. They can be used along with other inhibitors such as calcium gluconate, sodium molybdate, and trisodium citrate. Phosphonic acids show synergistic effects with these inhibitors. Various surface analysis techniques such as FTIR spectra, SEM, AFM, and EDAX have been used to analyze the nature of protective film formed on metal surface. Usually, the protective film consists of Fe^{2+} -phosphonic acid complex along with $Zn(OH)_2$ if Zn^{2+} is used. When phosphonic acids are used to prevent corrosion of iron, the adsorption process obeys Langmuir adsorption isotherm.

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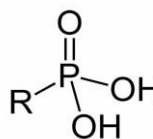
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Introduction

Phosphonic acids have been widely used as corrosion inhibitors¹⁻⁷⁷. Phosphonates or phosphonic acids are organic compounds containing $R-PO(OH)_2$ or $R-PO(OR)_2$ groups. Phosphonates are effective chelating agents that bind tightly to di- and trivalent metal ions, preventing them from forming insoluble precipitates (scale) and suppressing their catalytic properties. They are stable under harsh conditions. Phosphonates have a very strong interaction with surfaces, which results in a significant removal in technical and natural systems. Due to this strong adsorption, little or no remobilization of metals is expected. The hydrophobicity increased as the length of the alkyl group attached to the phosphonate head increases. Phosphonic acids tended to make tiles stain resistant, even after cleaning. On copper and steel, the phosphonic acids only slightly increased hydrophobicity. On the glass, the phosphonates bonded fairly poorly to the surface and slightly increased hydrophobicity.

Overall, all substances coated with the phosphonate SAM showed increased hydrophobicity⁷⁶. The adsorptive and inhibitive properties of some phosphonic acids have been studied in neutral aqueous solutions and to some extent in acidic solutions.

Structure of Phosphonic Acid



Commonly Used Organic Phosphonic Acids in Corrosion Inhibition

- ATMP: amino trimethylene phosphonic acid.
EDTMP: ethylene diamine tetra methylene phosphonic acid.
HEDP: 1-hydroxy ethylidene-1, 1-diphosphonic acid.
DTPMP: diethylene triamine penta methylene phosphonic acid.

Occurrence in Nature

The first naturally-occurring phosphonate, 2-amino-ethylphosphonic acid was identified in 1959 in plants and many animals, where it is localized in membranes. Phosphonates are quite common among different organisms from prokaryotes to eubacteria and fungi, mollusks, insects, and others. They were first reported in natural soils by Newman and Tate (1980).

Properties and Uses

Phosphonic acids have been used in metabolic regulation and in the development of potential drugs against several metabolic disorders. The great potential of these compounds in biological applications resulted in an intense effort

Table 1. The use of various phosphonic acids as corrosion inhibitors

No.	Metal	Medium	Inhibitor	Additive	Method	Findings	Ref
1.	Carbon steel	0.5 M HCl	hexamethylene diaminetetramethylphosphonic acid (HMDTMP)	-	Gravimetry, electrochemical measurements and surface morphological studies.	Mixed inhibitor, thermodynamic parameters, Langmuir adsorption isotherm.	1
2.	Carbon steel	120 ppm of CT and 73.58 ppm of sulphate ion	250 ppm of ethylphosphonic acid (EPA)	50 ppm of Zn ²⁺	Weight loss method, polarization study, AC impedance, FTIR, and UV-visible reflectance.	Anodic inhibitor, protective film consists of Fe ²⁺ -EPA complex.	2
3.	Ordinary steel	Simulated cooling water	7.5 · 10 ⁻⁵ to 1.10 ⁻³ phosphonate (PHOS)	cetyltrimethylammonium bromide (CTAB)	Weight loss, polarization curves, and electrochemical impedance spectroscopy	The inhibition efficiency decreased slightly with temperature as well as hold time immersion under open circuit potential conditions. The adsorption of PHOS on ordinary steel surface obeyed Langmuir's isotherm.	3
4.	Iron	3% NaCl	piperidin-1-yl-phosphonic acid (PPA) and (4-phosphonopiperazine-1-yl)phosphonic acid (PPPA)	-	Electrochemical studies, gravimetry, potentiodynamic polarization, weight loss method	Presence of PPA and PPPA increases the inhibition efficiency by decreasing the corrosion rate, adsorption of compounds tested on the Amoco iron surface obeys to Langmuir adsorption isotherm.	4
5.	Carbon steel	30 ppm of chloride	50 ppm of HEDP	zinc(II) ions (14, 20, and 30 ppm)	Weight loss method, X-ray photoelectron spectroscopy (XPS)	The results of the experimental surface analyses were compared to molecular modeling studies of the proposed HEDP-Fe(III)/Zn(OH) ₂ /HEDP-Zn(II) protective film. The increase in Zn(II) concentration leads to more compact and adherent film formation with decreased corrosion rates of carbon steel.	5
6.	Mild steel	Tap water	1-hydroxyethane-1,1-diphosphonic acid (HEDP)	calcium gluconate	Weight loss method, electrochemical polarization, and AC impedance measurements.	At higher concentrations (> 50 ppm), HEDP was found to be aggressive towards mild steel, but a formulation consisting of 25 ppm HEDP and 200 ppm calcium gluconate was found to protect mild steel effectively.	6
7.	Brass	Cooling water	Low phosphonic multipolymer	-	Weight loss method, energy-dispersion x-ray analysis (EDX), and electrochemical tests	Anodic reaction.	7
8.	Carbon steel	Rain water collected from roof top	250 ppm of amino (trimethylenephosphonic acid) (ATMP)	5 ppm Zn ²⁺	Polarization study, AC impedance and FTIR spectroscopy	Mixed inhibitor, protective film consists of Fe ²⁺ -ATMP complex and Zn(OH) ₂ .	8
9.	Carbon steel	1 M HCl	amino(trimethylene phosphonic acid) (ATMP)	-	Weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) techniques.	Mixed inhibitor, Langmuir adsorption isotherm, and physisorption process. This inhibitor can be also used as biocide; it has antibacterial effect against both gram-positive and gram-negative bacteria. The antibacterial activity of ATMP is a result of a combined effect of the pH solution and the chemical nature of the used phosphonate molecule.	9
10.	Carbon steel	-	250 ppm of ATMP	50 ppm of sodium tungstate and 10 ppm of Zn ²⁺	Potentiodynamic polarization study and FTIR spectroscopy.	Anodic inhibitor. Surface film has been analysed.	10
11.	Carbon steel	Low chloride aqueous medium	N,N-bis(phospho-nomethyl)glycine (BPMG)	tungstate and zinc ions	Potentiodynamic polarization and impedance studies, X-ray photoelectron spectroscopy (XPS), FTIR, and scanning electron microscopy (SEM).	Mixed inhibitor. Surface film is composed of iron oxides/hydroxides, zinc hydroxide, heteropolynuclear complex [Fe(III), Zn(II)-BPMG] and WO ₃	11
12.	Carbon steel	Low chloride environment	2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC)	ascorbate and Zn ²⁺	Potentiodynamic polarization studies, impedance studies, X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectrum.	Mixed inhibitor, presence of oxides/hydroxides of iron(III), Zn(OH) ₂ and [Zn(II)-PBTC-ascorbate] complex in the surface film.	12
13.	Carbon steel	Low chloride aqueous medium	ascorbic acid, 2-phosphonobutane-1,2,4-tri-carboxylic acid (PBTC), 1-hydroxy-ethane-1,1-diphosphonic acid (HEDP) and nitrioltris-(methylenephosphonic acid) (NTMP)	Zn ²⁺	Gravimetry, electrochemical impedance and potentiodynamic polarization studies, X-ray photoelectron and reflection absorption FTIR spectroscopy.	Ternary inhibitor. Surface films have been analysed.	13

Table 1 (cont.). The use of various phosphonic acids as corrosion inhibitors

No.	Metal	Medium	Inhibitor	Additive	Method	Findings	Ref
14.	Mild steel	Well water	1-hydroxyethane-1,1-diphosphonic acid (HEDP)	sodium tungstate, Zn^{2+}	AC impedance studies, potentiodynamic polarization studies, and reflection-absorption spectroscopy.	Anodic inhibitor. Surface films formed on mild steel exhibit high charge transfer resistance and low double layer capacitance, which suggests that the film is non-porous and hence protective.	14
15.	Carbon steel	60 ppm of Cl ⁻	Diethylenetriamine-pentamethylenephosphonic acid (DTPMP)	sodium gluconate, Zn^{2+}	Weight loss method, polarization study, AC impedance spectrum, atomic force micrographs, and FTIR spectra.	Mixed inhibitor. Protective film consists of Fe^{2+} -DTPMP complex, Fe^{2+} -SG complex, and $Zn(OH)_2$	15
16.	Polished zinc substrates	Na_2SO_4 Solution	1,5-diphosphono-pentane	-	EIS, XPS, and GD-OES data.	A simple oxide-hydroxide/diphosphonate model of the interface is proposed.	16
17.	Carbon steel	Natural seawater	thiomorpholin-4-yl-methyl-phosphonic acid (TMPA) and morpholin-4-methyl-phosphonic acid (MPA)	-	Potentiodynamic polarization study, FT-IR spectroscopy, scanning electron microscope, and energy dispersive X-ray analysis.	It shows that the addition of these molecules decreases the corrosion current density and the corrosion rate.	17
18.	Armco iron	3% chloride solution	piperidin-1-yl-phosphonic acid (PPA)	Zn^{2+}	Weight loss method, surface analysis, potentiodynamic polarization study, and Fourier transform infrared (FTIR) spectrum.	Synergistic effect exists between Zn^{2+} and PPA. Surface film analysis showed that in the absence of Zn^{2+} , the protective film consists of Fe^{2+} -PPA complex formed on the anodic sites of the metal surface, whereas in the presence of Zn^{2+} , the protective film consists of Fe^{2+} -PPA complex and $Zn(OH)_2$.	18
19.	Carbon steel	Cooling water	2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCa)	Polyvinylpyrrolidone (PVP)	Weight loss method, open circuit potential measurements, and potentiodynamic techniques.	A mixture of PBTCa and PVP acts as a synergic inhibitor and found to increase the inhibition efficiency to 96.7%.	19
20.	Carbon steel	Soft water	1-hydroxyethylidene-1,1-diphosphonic acid (HEDP)	silicate	Electrochemical impedance spectroscopy, scanning electron microscopy (SEM), Tafel polarization techniques.	Co-addition of 15 ppm HEDP and 15 ppm silicate has shown antagonistic behaviour. The surface homogeneity increases in case of inhibitors mixture application and this provides good protection to carbon steel against corrosion in soft water solution.	20
21.	Mild steel	Natural aqueous environment	3-vanillideneamino-1,2,4-triazole phospho-nate (VATP), 3-amisaldeneamino-1,2,4-triazole phosphonate (AATP) and 3-(p-nitrobenzylidene)amino-1,2,4-triazole phosphonate (PBATP)	cetyltrimethyl ammonium bromide (CTAB), sodium molybdate	Weight loss measurement, potentiodynamic polarization, AC impedance measurement, FTIR, XRD, and EDXA.	Addition of molybdate increases the inhibition efficiency of triazole in a synergistic manner. VATP as a better corrosion inhibitor for mild steel in aqueous solution. Additionally the formulation consisting of VATP, sodium molybdate, and CTAB offered good corrosion inhibition efficiency.	21
22.	Carbon steel	Epoxy resin	montmorillonite clay (MMT) with aminotrimethylphosphonic acid (ATMP)	-	X-ray diffraction, electrochemical impedance spectroscopy (EIS) and local electrochemical impedance spectroscopy (LEIS).	The corrosion resistance of the carbon steel coated by the epoxy resin containing ATMP-modified clay was higher than that obtained for the system containing non-treated clay. Local electrochemical measurements performed on scratched samples revealed the inhibitive role of ATMP at the carbon steel/coating interface.	22
23.	Aluminium	ethylene glycol-water mixtures	Ethylenediaminetetra-phosphonic acid (EDTPO)	-	Electrochemical and atomic force microscopy measurements.	Presence of EDTPO promotes the repairing of the passive film defects on the Al surface through a sealing process, which increases the stability of the oxide film layer. The film shows greater uniformity, lesser porosity, and remains stable for longer immersion periods as compared to those grown in the absence of EDTPO.	23
24.	304 stainless steel	Ground water	aminotrimethylidene-phosphonic acid (ATMP)	Zn^{2+} and polyoxyethylene sorbitan monooleate (Tween 80)	Luminescence spectra, FTIR spectra, XRD, XPS, and scanning electron microscopic studies.	A combined inhibition effect was achieved by adding both ATMP and Zn^{2+} along with Tween 80. The formulation functioned as a mixed-type inhibitor.	24

Table 1 (cont.). The use of various phosphonic acids as corrosion inhibitors

No.	Metal	Medium	Inhibitor	Additive	Method	Findings	Ref
25.	Carbon steel pipelines	Soft water	1-hydroxyethylidene 1,1-diphosphonic acid (HEDP)	sodium silicate	Electrochemical impedance, Tafel polarization measurements, scanning electron microscopy (SEM) and EDAX analysis.	The observed synergistic behaviour can be due to the incorporation of the silicate gel-like network through organic phosphorous bonds. The hydrodynamic condition of the electrolyte leads to enhancement of inhibition efficiency, which indicates that the corrosion inhibition was mass transfer controlled.	25
26.	Iron	3% NaCl	1-(4-methylpiperidine)methylene phosphonic acid (PO) and (1-(2'-aminoethylpiperidine))-2,2,4-tris(methylene-phosphonic acid) (3PO)	-	Micro-wave technique, IH-NMR, ¹³ C-NMR, 31P-NMR, Tafel polarization curves, weight loss techniques, and Fourier transform infrared spectroscopy (FTIR).	Adsorption of the inhibitors was found to follow the Langmuir's isotherm.	26
27.	Steel	Epoxy resin	polyaniline-amino trimethylene phosphonic acid (PANI-ATMP)	-	FTIR, UV and X-ray fluorescence, XRD, salt spray, open circuit potential measurement and EIS	CT resistance has been found to increase with time due to passivation of steel by PANI-ATMP pigment, indicating the protective nature of the coating.	27
28.	Carbon steel	60 ppm of Cl ⁻	2-chloroethylphosphonic acid (2-CIEPA)	Zn ²⁺	Polarization study, AC impedance spectra, and FTIR spectra.	Mixed inhibitor. Protective film consists of Fe ²⁺ -2-CIEPA complex and Zn(OH) ₂ .	28
29.	Carbon steel	Neutral aqueous environment	N-(2-hydroxyethyl) imino-bis(methylphosphonic acid) [HEIBMPA]	Zn ²⁺ and molybdate	Potentiostatic polarization study, reflection-absorption FTIR spectrum, and X-ray photoelectron spectra.	Ternary inhibitor system. The film consisted of [Fe(III)-HEIBMPA-molybdate] complex, [Fe(III), Zn(II)-HEIBMPA-molybdate] complex, oxides and hydroxides of iron and Zn(OH) ₂ .	29
30.	Brass	Synthetic water	Low phosphonic multipolymer	-	Weight loss measurements, electrochemical tests, potentiodynamic polarization, and energy-dispersive X-ray analysis (EDX).	Anodic inhibitor. The inhibition effects were due to the formation of a protective film of the multipolymer inhibitor on the metal surface.	30
31.	Carbon steel	Neutral aqueous environment	nitrotris(methylene-phosphonic acid) (NTMP)	Zn ²⁺ and ascorbate	Potentiostatic polarization studies, AC impedance studies, X-ray photoelectron spectrum, and reflection-absorption FTIR spectrum.	Mixed inhibitor. Surface film also supported the formation of insoluble complexes of phosphonate and ascorbate with metal ions as well as presence of Zn(OH) ₂ on the metal surface.	31
32.	Steel	1 M HCl	o-methyl-, o-ethyl and o-isopropyl-p-methoxy-phenyldithiophosphonic acid ammonium salts (MTPA, ETPA and IPTPA, resp.)	-	Tafel extrapolation, linear polarization techniques and current-potential curves	Surface coverage degrees indicate that the adsorption pattern is consistent with the Tomkin isotherm	32
33.	Carbon steel	Neutral oxygen-containing chloride solutions	1-hydroxyethylidene 1,1-diphosphonic acid (HEDP)	zinc	-	The predominant corrosion control mechanism of the zinc-HEDP mixture was on the anodic (metal dissolution) reaction. The effectiveness of the zinc-HEDP mixtures can enhance inhibition by increasing the zinc content of the mixture.	33
34.	Mild steel and copper	Cooling water	ATMP	cetyltrimethyl ammonium and cetyl pyridinium bromide (CTA and CPB)	Polarization studies.	The presence of biocide CTAB with inhibitor gives the inhibition efficiency of about 80% for mild steel. CPB with inhibitor shows higher interference between biocide and inhibitor, whereas CPB alone is found to act as an inhibitor for copper (73%), which shows that the inhibitor might interfere in the biocidal action on copper.	34
35.	Mild steel	Zinc ions	HEDP	-	Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).	The amount of zinc in the surface layer increases with Zn/HEDP molar ratio, which suggests the formation of either the 2:1 complex as well as Zn(OH) ₂ or the zinc salt of the complex.	35
36.	Carbon steel	Industrial water	ATMP	zinc sulfate	Immersion test.	The film to the surface of the material by affecting the early stage of film formation.	36
37.	Mild steel	Chloride media	2-carboxyethyl phosphonic acid (2-CEPA)	trisodium citrate and zinc ions	Weight-loss method and electrochemical impedance spectroscopy.	A combination of inhibitive ions such as citrate, 2-CEPA, and zinc ions at 25 ppm gives 96% inhibition efficiency and this corrosion inhibition is due to the formation of a protective film.	37

Table 1 (cont.). The use of various phosphonic acids as corrosion inhibitors

No.	Metal	Medium	Inhibitor	Additive	Method	Findings	Ref
38.	Carbon steel	Rain water	sodium dodecyl sulphate (SDS) and 1-hydroxyethane-1,1-diphosphonic acid (HEDP)	Zn ²⁺	Weight loss method and FTIR spectroscopy.	The protective film consists of Fe ²⁺ -SDS complex, Fe ²⁺ -HEDP complex, and Zn(OH) ₂ . The HEDP-Zn ²⁺ system shows good IE. The protective film consists of Fe ²⁺ -HEDP complex and Zn(OH) ₂ .	38
39.	Copper	Neutral aqueous solution	3-benzylideneamino-, 3-cinnamylideneamino-, 3-salicylideneamino-, and 3-(p-nitro)benzylideneamino-1,2,4-triazole phosphonate (BAPT, CATP, SATP and PBATP)	biocide	Polarization, impedance measurements, FTIR, XRD, and EDXA	The protective film formed on the metal surface.	39
40.	Mild steel	Neutral oxygen-containing solutions	1-hydroxyethylidene-1,1-diphosphonic acid (HEDP)	zinc and calcium	Electrochemical study.	Low stability of calcium complexes compared with ferrous complexes, which facilitates the displacement of calcium ions from their complexes by ferrous ions forming soluble, unprotective, ferrous complexes. The zinc-HEDP mixtures give effective inhibition at zinc.	40
41.	Sol-gel film on aluminium	Organic anions	phenylphosphonic acid (PPA)	-	Potentiodynamic polarization and electrochemical noise measurements, scanning electron microscopy (SEM) and Auger electron spectroscopy (AES).	phenyltrimethoxysilane (PTMOS) based sol-gel film due to π -interactions, the organic phosphonate adds to the protection efficiency of the sol-gel film	41
42.	Mild steel	Industrial hard water containing 3·10 ⁻² M Ca ²⁺ ions	HEDP	sodium metasilicate pentahydrate Na ₂ SiO ₃ ·5H ₂ O	Electrochemical measurements, mass-loss measurements, SEM, and EDX.	The mixture (1.7x10 ⁻⁵ M HEDP + 2.6x10 ⁻³ M SiO ₂) in the Ca ²⁺ containing electrolyte is shown to be able to inhibit efficaciously the corrosion of iron at room temperature, considering uniform corrosion at pH 7 or pitting corrosion at pH 11.	42
43.	Carbon steel	Chloride solution	N-phosphonomethyl-glycine (NPMG)	Zn ²⁺	Polarization, electrochemical impedance measurements, XPS, and AES spectra.	Films consisted of hydrous ferric oxides (Fe(OH) ₃ and FeOOH) with small amounts of Fe-NPMG complex, ZnO, and corrosion products.	43
44.	Copper	Neutral aqueous environment	3-vanillydeneamino and 3-anisalideneamino-1,2,4-triazole phosphonate (VATP and AATP)	-	Potentiodynamic polarization measurement and electrochemical impedance spectroscopy (EIS).	VATP showed better protection over the other inhibitors used. The dissolution of copper in presence of VATP and AATP with biocide mixture is negligible compared to blank.	44
45.	Mild steel	Natural aqueous environment	3-salicylideneamino-1,2,4-triazole phosphonate (SATP)	-	Weight loss, potentiodynamic polarization, and AC impedance methods.	SATP was found to be the best corrosion inhibitor compared to the other compounds.	45
46.	Mild steel	Natural aqueous environment	3-benzylideneamino, 3-cinnamylideneamino and 3-anisalideneamino-1,2,4-triazole phosphonate (BAPT, CATP and AATP, resp.)	Mo and CTAB	Weight loss and electrochemical polarization techniques.	The formulation consisting of AATP, Mo and CTAB offered good corrosion inhibition efficiency	46
47.	Iron	NaCl	piperidin-1-yl-phosphonic acid (PPA) and (4-phosphono-piperazin-1-yl) phosphonic acid (PPPA)	-	Electrochemical measurements and potentiodynamic polarization studies.	PPPA has a strongly inhibitive effect on chloride pitting corrosion. It seems that the addition of the NCH ₂ PO ₃ H group (center adsorption) in the PPA para-position, giving PPPA, reinforces the active sites of this molecule and consequently increases its inhibition efficiency.	47
48.	Mild steel	0.1 M HCl	3-benzylideneamino and 3-cinnamylidene-amino-1,2,4 triazole phosphonate (BAPT and CATP, resp.)	-	Weight loss and polarization measurements.	Mixed-type inhibitors. Langmuir adsorption isotherm.	48
49.	Carbon steel	Chloride solutions	N-phosphonomethyl-glycine (NPMG)	Zn ²⁺	Electrochemical impedance measurements.	At the corrosion potential, electrochemical impedance diagrams exhibited a high frequency loop, which was ascribed to the charge transfer process, and a low frequency loop that was related to diffusion across the protective film. Analysis of impedance spectra in terms of an equivalent circuit model showed that the corrosion behaviour of the metal - layer solution system was strongly dependent on the physicochemical properties of the corrosion products - corrosion inhibitor porous layer	49

Table 1 (cont.). The use of various phosphonic acids as corrosion inhibitors

No.	Metal	Medium	Inhibitor	Additive	Method	Findings	Ref
50.	Carbon steel	Chloride solution	HEDP	Zn ²⁺	-	The protective film consists of Fe ²⁺ -HEDP complex and Zn(OH) ₂ .	50
51.	Carbon steel	Neutral medium	DTPMP	Zn ²⁺	Vollammetric, gravimetric, and electrochemical methods.	The corrosion inhibition efficiency of DTPMP+ Zn ²⁺ is found to be 80% after 24 hours.	51
52.	Mild steel	60 ppm chloride	sodium salt of HEDP	Zn ²⁺	UV-visible, FTIR, and luminescence spectroscopy.	Presence of Zn ²⁺ facilitates the transport of HEDP from the bulk of the solution to the metal surface; both the anodic reaction and cathodic reaction are controlled effectively.	52
53.	Carbon steel	Chloride ions	HEDP	sodium molybdate and zinc	-	Presence of more than 1,200 ppm of chloride ions, temperatures greater than or equal to 42.5°C, the combination of HEDP, molybdate and zinc could not control the corrosion in a cooling water system	53
54.	Carbon steel	60 ppm chloride ion	phosphonates	Zn ²⁺	Polarization and weight loss method.	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.	54
55.	Mild steel	polyaniline (PANI)	sulfonic acid and phosphonic acid	-	Scanning reference electrode technology (SRET).	A qualitative model is proposed, which entails passivation of the metal surface through anodization of the metal by PANI and formation of an insoluble iron-dopant salt at the metal surface.	55
56.	Carbon steel	200 ppm NaCl	fatty amines in association with phosphonocarboxylic acid	-	Steady-state current-voltage curve, electrochemical impedance measurement, and x-ray photoelectron spectroscopy (XPS).	Anodic inhibitor. The film was composed of an iron oxide/hydroxide mixture incorporating the organic compounds. The inhibitive molecules interact with the iron oxides.	56
57.	304 stainless steel	Ground water	100 ppm of 3-phospho-nopropionic acid and 150 ppm of Tween 80 (polyoxyethylene sorbitan monooleate)	50 ppm of Zn ²⁺	Luminescence, XRD, FTIR spectra, pit morphology, and scanning electron microscopy.	Mixed inhibitor.	57
58.	304 stainless steel	Ground water	3- phosphonopropionic acid (3-PPA) and Triton X-100.	Zn ²⁺	Open circuit potential-time, polarization, impedance, and luminescence measurements.	The nature of the film formed and the mechanistic aspects of film formation has been analysed.	58
59.	Mild steel	60 ppm Cl ⁻	1-hydroxyethane-1,1-diphosphonic acid (HEDP)	oCarboxymethyl cellulose (CMC) and Zn ²⁺	Weight loss study, X-ray diffraction (XRD), FTIR and polarization study.	The protective film consists of Fe ²⁺ - HEDP complex, Fe ²⁺ -CMC complex, and Zn(OH) ₂ .	59
60.	Mild steel	Oxygen containing aqueous solutions	HEDP	Zn ²⁺	-	Anionic complex can behave as an anodic, passivating inhibitor at a concentration as low as 0.00015M (20 ppm zinc-32 ppm HEDP mixture).	60
61.	Aluminum	Neutral aqueous chloride solutions	morpholinemethylene-phosphonic acid (MMPA)	-	Direct current and alternating current techniques.	The adsorption of MMPA on aluminum oxide (Al ₂ O ₃) prevents the adsorption of chloride ions and leads to the formation of an insoluble aluminum complex of MMPA, which explains the significant decrease of the aluminum dissolution rate in the aggressive medium.	61
62.	Steel	Oxygen saturated environment	tartrate with organophosphonic acid (2-carboxyethylphosphonic acid)	zinc	Weight change method, polarization, AC impedance technique, UV-VIS reflectance, UV-VIS luminescence, and ESCA techniques	The protective film has been analysed.	62
63.	Iron	-	N,N-di(phosphono-methyl)glycine (DPMG)	bivalent cations (Ba ²⁺ , Sr ²⁺ , Ca ²⁺ and Zn ²⁺)	Atomic force microscopy and X-ray photoelectron spectroscopy (XPS).	The surface layer was composed of a mixture of slightly soluble Zn ²⁺ /DPMG and zinc hydroxide.	63

Table 1 (cont.). The use of various phosphonic acids as corrosion inhibitors

No.	Metal	Medium	Inhibitor	Additive	Method	Findings	Ref
64.	Carbon steel	60 ppm Cl ⁻	Carboxymethylphosphonic acid (CMPA) and 2-carboxyethylphosphonic acid (2-CEPA)	Zn ²⁺	Weight loss method, X-ray diffraction, Fourier transform infrared, and luminescence spectroscopy.	The protective film is found to consist of Fe ²⁺ -phosphonate complex and Zn(OH) ₂ ; it is found to be luminescent.	64
65.	Mild steel	60 ppm Cl ⁻	ethylphosphonic acid (EPA)	Zn ²⁺	Weight loss method, polarization study, and X-ray diffraction.	Mixed inhibitor.	65
66.	Mild steel	60 ppm Cl ⁻	ethyl and 2-carboxy-ethyl phosphonic acid (EPA and 2-CEPA, resp.)	Zn ²⁺	Polarization study and fluorescence Spectra.	Mixed inhibitor.	66
67.	Carbon steel	60 ppm Cl ⁻	2-chloroethyl phosphonic acid (2-Cl EPA)	Zn ²⁺	UV-luminescent.	The protective film consists of Fe ²⁺ -2-Cl EPA complex and Zn(OH) ₂ .	67
68.	0Cr13 stainless steel	H ₂ SO ₄ solutions	N-sulfonated amino-dimethylene-phosphonic acid (SADP) compared with HEDP (1-hydroxy-ethylidene-1,1-diphosphonic acid and amino-trimethylene phosphonic acid (ATMP))	-	Linear polarization and anodic polarization curve methods.	Langmuir adsorption isotherm.	68
69.	Mild steel	60 ppm Cl ⁻	HEDP	Zn ²⁺	Weight-loss study, UV-visible reflectance spectroscopy and X-ray diffraction.	Mixed inhibitor	69
70.	Steel	saturated Ca(OH) ₂ solution	nitrotris(methylene-phosphonic acid) (NTMP)	-	Polarization measurement, Fourier transform infra-red spectroscopy, and X-ray photoelectron spectroscopy	Langmuir adsorption isotherm.	70
71.	Carbon steel	60 ppm Cl ⁻	2-chloroethyl phosphonic acid (2-Cl EPA)	Zn ²⁺	Weight-loss, electrochemical methods, polarization study, UV-visible absorption, and reflectance spectra.	Mixed inhibitor. The protective film consisted of Fe ²⁺ -2-Cl EPA complex, Zn(OH) ₂ and oxides of iron. The film was found to be semiconducting in nature.	71
72.	Armco iron	H ₂ SO ₄	aminophosphonic acids	halide ions	Polarization measurement, scanning electron microscopy, FTIR reflection-absorption and X-ray photoelectron spectroscopy techniques.	The inhibition efficiency of aminophosphonic acids can be increased by halide ions. In the presence of aminophosphonic acids, the anomalous behavior of halide ions can be eliminated during anodic polarization.	72
73.	Carbon steel	low chloride aqueous environment	N,N-bis(phosphono-methyl)glycine (BPMG)	zinc	Potentiodynamic polarization, X-ray photoelectron spectroscopic analysis (XPS), dDeconvolution and FTIR spectroscopy, SEM.	Film showed the presence of the elements iron, phosphorus, nitrogen, oxygen, carbon, and zinc. Deconvolution spectra of these elements in the surface film showed the presence of oxides/hydroxides of iron(III), Zn(OH) ₂ , and [Zn(II)-BPMG] complex.	73
74.	Carbon steel	1.0 M HCl solution	hexamethylenediamine tetra(methylene phosphonic acid) (HMDTMPA)	-	Weight loss measurement, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) techniques, and scanning electron microscope (SEM)	Langmuir's adsorption isotherm.	74
75.	Iron	3% sodium chloride	thiomorpholin-4-yl-methylphosphonic acid (TMPA) and morpholin-4-yl-methyl-phosphonic acid (MPA)	-	NMR and IR spectroscopy, Tafel polarization curve, weight loss technique, and FTIR spectroscopy	Langmuir's isotherm.	75

directed to the development of efficient synthetic methods for their preparation, with particular attention to stereoselective synthesis. Phosphonic acids are also used as corrosion inhibitors in concrete, coatings, rubber blends, anti-freeze coolants, ship ballast compartments, preservation of organic products, coal slurries, etc⁷⁷. Phosphonic acids are also good complexing agents. Among other phosphonic acids, diethylene triamine penta methylene phosphonic acids in particular can be used as scale and corrosion inhibitor in circulating cool water system and boiler water, and especially good in alkali circulating cool water system without additional pH regulation. It can also be used as scale and corrosion inhibitor in oilfield refill water, cool water and boiler water with high concentration of barium carbonate. It can also be used as peroxide stabilizer, chelating agent in weaving and dyeing industry, pigment dispersant, microelement's carrying agent in fertilizer and concrete modifier. In addition, DTPMPA is used in papermaking, electroplating, acid cleaning and cosmetics. Various phosphonic derivatives are widely used chemicals for corrosion inhibition in neutral aqueous solutions. Phosphonic acids find wide application in the corrosion protection of various metals in different environment.

Review and Discussion

The use of phosphonic acids as corrosion inhibitors are discussed in the following section.

Metals

Phosphonic acids have been used to control the corrosion of various metals such as mild steel¹⁻⁶, brass^{7,30}, copper^{34,39,44}, aluminium^{23,61}, stainless steel^{24,57,58,68}, sol-gel film on aluminium⁴¹, Armco iron^{18,72}, and zinc¹⁶.

Medium

The inhibition efficiency of phosphonic acids in controlling corrosion of metals in various environments has been investigated. Acidic medium^{1,9,32,48,68,72,74}, alkaline medium^{2,4,5,11-13,15,16,18}, and neutral medium^{3,6-8,14,17,19-21} have been used for this purpose.

Inhibitor

Phosphonic acids have been used alone or in combination with other inhibitors such as Zn^{2+2,5,8,14,15,18}, CTAB^{3,21,34,46}, calcium gluconate⁶, tungstate¹¹, ascorbate¹², silicate^{20,25}, sodium molybdate^{21,29,31,53}, and trisodium citrate³⁷.

Methods

Various methods have been used to evaluate the inhibition efficiency of phosphonic acids. Weight-loss method²⁻⁷, Electrochemical studies (polarization and AC impedance)^{1-4, 6-12}, FTIR spectra^{2,8,10-13}, UV-visible reflectance spectra^{2,14,24}, XPS^{5,11-13} and surface analysis by SEM^{11,20,24,25}, AFM⁶³, and EDX^{7,21,25,30}.

Findings

Using phosphonic acids as inhibitor, above studies have been conducted and following findings were reported:

Isotherm: Generally, the adsorption of phosphonic acids on metal surface obey Langmuir adsorption isotherm as supported by the studies of Laamari et al, Tourir et al, and Amar et al^{1,3,4,26}; and Temkin isotherm as supported by Karakus et al³². Adsorption of phosphonic acids on metals like iron, carbon steel obey adsorption isotherm.

Type of inhibitor: Phosphonic acids have been used as mixed inhibitor^{1, 8, 9, 11, 12} and anodic inhibitor^{2, 10, 14, 30}.

Nature of protective film: The protective films formed on metal surface when phosphonic acids are used as corrosion inhibitors have been analyzed by FTIR, UV, SEM, AFM, and XPS. It is observed that the protective films consists of Fe²⁺ inhibitor complex is formed on anodic sites of the metal surface and Zn(OH)₂ formed on the cathodic sites of the metal surface^{2, 10, 12}.

The use of various phosphonic acids as corrosion inhibitors are summarized in Table 1 above.

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