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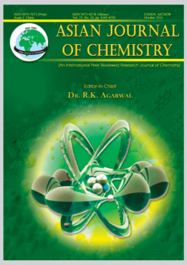

REVIEW

Phosphonic Acids used as Corrosion Inhibitors-A Review

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Inhibition of corrosion and scaling can be done by the application of inhibitors. It is noted that the effect of corrosion inhibitors is always caused by change in the state of surface being protected due to adsorption or formation of hardly soluble compounds with metal cations. Several phosphonic acids have been used as corrosion inhibitor along with metal cation such as Zn^{2+}. The synergistic effect between the inhibitors gives the more inhibition efficiency. Phosphonic acids are inhibitors, which have been used due to their stability, ability to form complexes with metal cations. They are adsorbed on metal surface through these polar atoms. The adsorption obeys various adsorption isotherms. The film have been analyzed by many technologies such as, FTIR, SEM, UV-Visible spectra, EIS and electrochemical studies like polarization and AC impedance.

Key Words: Phosphonic acid, Synergism, Eco-friendly inhibitors, Metal cations.

INTRODUCTION

Use of some inhibitors such as chromate, has been banned because of toxicity and environmental damage they create. So the use of eco-friendly, less toxic and non-toxic materials like phosphonic acid is used as corrosion inhibitors[1-53]. The phosphonic acid containing atoms such as N, P, O. Theses atoms coordinate with the corroding metal atoms(their ion), through their electrons. Hence the protective films are formed on the metal surface and hence corrosion is prevented.

Phosphonic acids have been used as corrosion inhibitors due to their hydrolytic stability, ability to form a complex with metal ions and scale inhibiting properties. It is eco-friendly, non-toxic and relatively less expensive. They are easily biodegradable also. However, this biodegradability limits the storage and long-term usage of phosphonic acid. However, it is proposed that the decomposition by phosphonic acid by microorganisms can be prevented by addition of biocide such as *N*-cetyl-*N, N, N*- trimethyl ammonium bromide.

Metals: The phosphonic acids have been used to control the corrosion of various metals such as mild steel[3,4,6-23,26,29,35,46,49], carbon steel[1,2,5,27,28,31-34,36,37,38,41,44,45,47,48,50-53], ARMCO iron[24,39, 43], iron[30], aluminium[40], stainless steel[25] and 304 stainless steel[42].

Medium: The inhibition efficiency of phosphonic acids, in controlling corrosion of metals in various medium such as neutral chloride medium[1,4,6,8,9-11,13-19,21,22,24-29,32-35,37,38,41,44,47], low chloride medium[3,7,12,20,23,28,45], acidic medium[51,52,53], rain water[36,46], well water[48,49,50], artificial sea water[30,39,43], industrial hard water[31], have been used for this purpose.

Additives: Phosphonic acids have been used as corrosion inhibitor, alone or in combination with other additive such as Zn^{2+}[2-14,16,18,19-27,29,32-38 42-50], PAA[6,16,18,39], molybdate[10,13,38], sodium tungstate[48,49,50], ascorbate[33,45], sodium gluconate[47], calcium gluconate[3], sodium tartoborate[40], sodium silicate[41], CTAB[8], SDS[36]), Ba^{2+}[24], Sr^{2+}[24], MOP[28], Tween 80[42].

Temperature: The inhibition efficiency of phosphonic acids have been evaluated at room temperature[1-51,53] and also at high temperature[52].

Methods: Various methods have been used to evaluate the inhibition efficiency of phosphonic acids usually, weight-loss method[1,3,4,6-9,11-17,19,20,22,23,25-27,31,32,35,36, 39,45,47-52], electrochemical studies (polarization and AC impedance)[1-4,6,7-9,17,18,21,22,24,25,27,28-31,33,34,36,38,39,41,43,44,46,47-52], voltametric and gravimetric methods[29,39,53], study state current voltage[2,4] methods have been employed.

Adsorption isotherms: The adsorption behaviour of the phosphonic acid onto the metal surface has been investigated, the type of adsorption isotherm has been proposed *e.g.*, Langmuir adsorption isotherm[39,51,52].

Surface analysis: The protective film formed on the metal surface, during the process of corrosion protection of metals by phosphonic acid, have been analyzed by various surface analysis techniques such as AFM[24,40,47], SEM[39,41,42,44,52], FTIR[4,8,10-16,18,21,22,26,33,34,36,38,42-50], XRD[4,5,8,9,11,12,14-16,20,23,42]), XPS[2,5,24,32,33,38,44,45], UV-Visible spectra[6,9,11,12,14,18,20,23,26], ESCA[7,25], EDAX[41], UV-Visible NIR[9]. In general, it has been observed that the protective film consists of the metal- active principle complex. In some cases, $Zn(OH)_2$ is deposited on the cathodic sites of the metal surface, if Zn^{2+} is used along with the phosphonic acid.

Phosphonic acid: Phosphonic acids have been used as corrosion inhibitors. Amine derivatives[4,6,9,10,13,17,29], alkyl and aryl derivatives[11,12,16], carboxy derivatives[3,7,22,25,35], hydroxy derivatives[1,8,14,15,20,21,23,26,31,36,37,41,49], have been used as a corrosion inhibitors.

A list of phosphonic acids that have been used as corrosion inhibitors is given in Table-1.

TABLE-1
PHOSPHONIC ACIDS USED AS CORROSION INHIBITORS

S. No	Metal	Medium	Inhibitor	Additive	Methods	Findings	Ref. no
1	Carbon steel	Neutral solution	1-Hydroxyethane-1,1-diphosphonic acid (HEDP)		Weight loss, polarization, impedance study.	At low concentrations, HEDP inhibits carbon steel corrosion by a precipitation mechanism. Increasing HEDP concentration beyond the optimal value decreases its inhibition efficiency due to the dissolution of the oxide layer.	1
2	Carbon steel	0.5 M NaCl	Phosphonic acid	Zn^{2+}	Steady state current voltage, AC impedance, polarization, XPS.	Better inhibition efficiency was found. XPS shows the constituents of the film like Zn, P & O.	2
3	Mild steel	Low chloride medium	2-Carboxyethyl phosphonic acid (2-CEPA)	Zn^{2+}, Calcium Gluconate	Weight loss, electrochemical studies	Synergistic effect found. It shows better inhibition efficiency.	3
4	Mild steel	60 ppm Cl^-	Aminotrimethylidene phosphonic acid (ATMP)	Zn^{2+}	Weight loss, potentiostatic polarization, XRD, FTIR.	The formulation acts as a anodic inhibitor. The protective film formed on the surface to be found luminescent.	4
5	Carbon steel		Phosphonic acid	Zn^{2+}	Steady state current voltage, EIS, XPS, reflection adsorp-tion spectroscopy	XPS and reflection and adsorption spectroscopy shows the synergistic effect. The inhibitor film act as protective layer impermeable to ionic or molecular diffusion.	5
6	Mild steel	Neutral chloride	Amino(trimethylene phosphonic acid) (ATMP)	Zn^{2+} Polyacrylamide (PAA)	Weight loss, X-ray diffraction, FTIR, UV-Visible, electrochemical studies	Controls the anodic reactions.	6
7	Mild steel	Low chloride medium	2-Carboxyethyl phosphonic acid (2-CEPA)	Zn^{2+}	Weight loss, electro chemical study, ESCA.	The dissolution of iron was controlled by the diffusion of iron phosphonate soluble complex and H+ ions through this inhibitor film.	7
8	Mild steel	Neutral aqueous environment	1-Hydroxyethane-1,1-diphosphonic acid (HEDP)	Zn^{2+}, CTAB	Weight loss, FTIR, XRD, polarization	The synergistic effect is offered between the inhibitor and Zn^{2+}. 100 % biocidal efficiency was found. The protective layer found to be luminescent.	8
9	Mild steel	60 ppm Cl^-	Citrate ethylene diamine phosphonic acid (CEDPA)	Zn^{2+}	Weight loss, polarization, EIS, XRD, UV-Visible-NIR spectra.	Synergism is existing between the inhibitors. The formulation functions as a mixed inhibitor.	9
10	Mild steel	60 ppm Cl^-	Amino(trimethylene phosphonic acid) (ATMP)	Zn^{2+}, MoO_4^{2-}	XRD, FTIR, luminescence spectra.	Better IE found with this combination.	10
11	Mild steel	Neutral chloride	Phenyl phosphonic acid (PPA)	Zn^{2+}	Weight loss, UV - Visible and FTIR	Only phosphonate group coordinate with Zn and Fe.	11
12	Mild steel	Low chloride	Ethyl phosphonic acid (EPA)	Zn^{2+}	Weight loss, UV, XRD, FTIR, luminescent spectra.	The protective film formed on the surface to be found luminescent.	12
13	Mild steel	Neutral aqueous environment	Aminotrimethylidene phosphonic acid (ATMP)	Zn^{2+}, Molybdate.	Weight loss, FTIR.	The best IE was found. It controls both the anodic and cathodic reaction.	13
14	Mild steel	Neutral aqueous environment	1-Hydroxyethane-1,1-diphosphonic acid (HEDP)	PAA, Zn^{2+}.	Weight loss, XRD, UV-Visible reflectance, FTIR and luminescence spectra	The film formed was found to be luminescent.	14

S. No	Metal	Medium	Inhibitor	Additive	Methods	Findings	Ref. no
15	Mild steel	60 ppm Cl^-	1-Hydroxyethane-1,1-diphosphonic acid (HEDP)		Weight loss, XRD, FTIR.	The better inhibition efficiency was found. The film formed was found to be luminescent.	15
16	Mild steel	60 ppm Cl^-	Phenyl phosphonate (PPA)	Polyacrylamide (PAA) , Zn^{2+}	Weight loss, FTIR, XRD.	Synergistic effect existing between the inhibitors. 50 ppm PAA and 300 ppm PPA shows an antagonistic effect.	16
17	Mild steel	60 ppm Cl^-	Tartrate-ethylene diamine phosphonic acid (TEDPA)		Weight loss method, Electrochemical techniques.	This polymer when used alone, accelerated corrosion, but offered good inhibition in the presence of zinc ions	17
18	Mild steel	60 ppm Cl^-	Phenyl phosphonic acid (PPA)	Zn^{2+}, polyacrylamide (PAA)	Electrochemical studies, FTIR and UV	Mixed inhibitor	18
19	Mild steel	Neutral aqueous environment	2-Chloroethyl phosphonic acid (2-Cl EPA) and ethyl phosphonic acid (EPA)	Zn^{2+}	Surface studies, Weight loss method and Luminescent spectra.	2-Cl EPA has more inhibitive property than the EPA.	19
20	Mild steel	Low chloride	1-Hydroxyethane-1, 1-diphosphonic acid (HEDP)	Zn^{2+}	Weight loss, UV visible, XRD.	Has no influence on the biocidal efficiency of CTAB. Protective film consists of iron phosphonate.	20
21	Mild steel	Neutral aqueous environment	1-Hydroxyethane-1, 1-diphosphonic acid (HEDP)	Zn^{2+}	Polarization and FTIR	The formulation acts as a mixed inhibitor. The film was found to be luminescent.	21
22	Mild steel	60 ppm Cl^-	2-Carboxyethyl phosphonic acid (2 CEPA), ethyl phosphonic acid (EPA)	Zn^{2+}	Weight loss, Electro chemical study, FTIR.	2-CEPA has better IE than the EPA. Film found to be luminescent. IE decreases as the immersion period increases.	22
23	Mild steel	Low chloride medium	1-Hydroxyethane-1, 1-diphosphonic acid (HEDP)	Zn^{2+}	Weight loss, XRD, UV- Visible reflectance spectra.	Synergism has been calculated between HEDP and Zn^{2+} ion. The system functions as a mixed inhibitor.	23
24	ARMCO Iron	Neutral solution	*N,N*-di(phosphonomethyl) glycine (DPMG)	Ba^{2+}, Sr^{2+}, Zn^{2+}	Polarization, XPS, AFM.	Influence of bivalent cations like Ba^{2+}, Sr^{2+}, Zn^{2+} was studies. Synergism is existing between the inhibitors. Ba^{2+} with an inhibitor form smooth, rigid, layer with very few pores with high resistance. Zn^{2+} forms instant layer.	24
25	Stainless steel	Neutral environment	2-Carboxyethyl-phosphonic acid (2-CEPA)	Zn^{2+}	Weight loss method, AC impedance, ESCA, UV- Visible spectra.	The composition of protective layer was analyzed by ESCA. Better inhibition Efficiency was observed.	25
26	Mild steel	60 ppm Cl^-	1-Hydroxyethane-1,1-diphosphonic acid (HEDP)	Zn^{2+}	Weight loss method, FTIR, UV- Visible spectra	The best IE was found. It controls both the anodic and cathodic reaction.	26
27	Carbon steel	60 ppm Cl^-	Phosphonates	Zn^{2+}	Wright loss, Polarization.	Phosphonates functions as transporters. Zn^{2+}- transporting ability dominant than the size of the Fe^{2+} - phosphonates complexes.	27
28	Carbon steel treated by MOP TDP.	0.1 M NaCl	Tridecyl phosphonate (TDP)	Methacryloxyethyl phosphonate (MOP)	IR, Electrochemical Impedance Spectroscopy	Synergism is existing between the inhibitors. Good protection is obtained by the mixture of 5 % TDP with 1.5 % of MOP.	28
29	Mild steel	Neutral medium	Diehtylenetriaminepenta (methylene phosphonic acid (DTPMP)	Zn^{2+}	Voltammetric, gravimetric and electrochemical methods.	Better inhibition efficiency was found.	29
30	Iron	3 % NaCl	Piperidin-1-yl-phosphonic acid (PPA), (4-phosophono-piperazin-1-yl) phosphonic acid (PPPA)		Polarization	Better IE found for PPPA than the PPA. Addition of phosphonic acid reduces the accessibility of Cl^- ions.	30

S. No	Metal	Medium	Inhibitor	Additive	Methods	Findings	Ref. no
31	Carbon steel	Industrial hard water	1-Hydroxyethane-1,1-diphosphonic acid (HEDP)	Na_2SiO_3. $5H_2O$ and Ca^{2+}	Weight loss, AC impedance, EDSX, SEM and various pH.	Observed better IE. Synergism is found.	31
32	Carbon steel	Neutral chloride solution	*N*-phosphono-methyl-glycine (NPMG)	Zn^{2+}	Weight loss, EIS, XPS.	Polarization curves shows that NPMG/Zn^{2+} mixture retarded both the anodic and cathodic partial reaction. Films consisted mainly of hydrous ferric oxides ($Fe(OH)_3$ and FeOOH). AES depth profiling showed that the most protective surface film was thicker.	32
33	Carbon steel	Neutral aqueous environment	Nitrilotris(methylenephosphonic acid) (NTMP)	Zn^{2+}, ascorbate	Impedance studies, X-ray photoelectron, FTIR	The synergism is found between the inhibitors. The mixed inhibitors.	33
34	Carbon steel	60 ppm Cl^-	Disodium hydrogen phosphate (DSHP)	Zn^{2+}	AC Impedance and FTIR.	The formulation acts as a mixed inhibitor. The Synergism is existing.	34
35	Mild steel	Neutral chloride	2-Carboxyethyl phosphonic acid (2 CEPA)	Zn^{2+}	Weight loss, EIS.	EIS shows the citrate based inhibitor system is multilayer. The resistance of the first layer due to the cross- linked iron - corrosion inhibitive film formation.	35
36	Carbon steel	Rain water	1-Hydroxyethane-1,1-diphosphonic acid (HEDP)	SDS, Zn^{2+}	Weight loss, AC impedance, polarization, FTIR.	SDS, SDS-Zn^{2+} accelerate the corrosion rate. HEDP-SDS-Zn^{2+} formulation show excellent IE. Synergism between the inhibitors.	36
37	Carbon steel	Neutral oxygen-containing chloride solution	1-Hydroxyethane-1,1-diphosphonic acid (HEDP)	Zn^{2+}		Inhibition by these mixtures depended not only on the zinc/HEDP molar ratio but also on the concentration of both zinc and HEDP.	37
38	Carbon steel	Neutral aqueous environment	*N*-(2-hydroxyethyl) iminobis(methylenephosphonic acid (HEIBMPA)	Zn^{2+} Molybdate	Potentiostatic polarization, FTIR, XPS.	Increase in R_p value indicates the formation of non-porous protective film. Synergism between the inhibitors.	38
39	ARMCO iron	3 % NaCl	Piperidin-1-yl-phosphonic acid (PPA), (4-Phosophono-piperazin-1-yl) Phosphonic acid (PPPA)		Weight loss, polarization, gravimetric and electrochemical techniques, SEM, temperature studies.	It obeys Langmuir's adsorption isotherm. The adsorption on active sites of a metal surface suppressing the dissolution reaction.	39
40	Al	Ethyleneglycol- water mixture	Ethylenediaminetetraphosphonic acid (EDTPO)	8.4 pH, sodium tartaborate.	AFM	The presence of this inhibitor promotes the repairing of passive film defects on Al surface.	40
41	Carbon steel	Neutral and aerated soft water	1-Hydroxyethane-1, 1-diphosphonic acid (HEDP)	Sodium silicate	SEM, EIS, polarization, EDAX.	Mixed inhibitor. EDAX shows incorporation of HEDP as phosphorous bonds through the silicate gel like network.	41
42	304 stainless steel	Ground water	Aminotrimethylidene phosphonic acid (ATMP)	Zn^{2+}, Polyoxyethylene sorb-itan mono-oleate (tween 80)	Luminescence spectra, FTIR spectra, XRD, XPS and SEM.	The formulation functioned as mixed type inhibitor. Synergistic effect is observed between the inhibitors.	42
43	ARMCO iron	3 % NaCl	Piperidin-1-yl-Phosphonic acid(PPA)	Zn^{2+}	Potentiodynamic polarization, FTIR.	The synergistic effect is offered between the inhibitor and Zn^{2+}	43
44	Carbon steel	Natural sea water	Thiomorpholin-4ylmethylphosphonic acid (TMPA), morpholin-4-methyl-phosphonic acid (MPA)		Polarization, FTIR, SEM XPS	It gives bonding mechanism between the metallic surface and the inhibitors.	44
45	Carbon steel	Low chloride	*N,N-bis*(phosphonomethyl) glycine (BPMG)	Zn^{2+}, Ascorbate.	Weight loss, XPS, FTIR.	Formulation acts as a mixed inhibitor. The ternary inhibitor formulation is found to be effective in the pH range 5–11	45

S. No	Metal	Medium	Inhibitor	Additive	Methods	Findings	Ref. no
46	Mild steel	Rain water	Diehtylenetriaminepenta (methylene phosphonic acid (DTPMP)	Zn^{2+}	AC impedance, FTIR, AFM.	Nano film formed on the metal surface was found.	46
47	Carbon steel	60 ppm Cl^{-}	Diehtylenetriaminepenta (methylene phosphonic acid (DTPMP)	Zn^{2+}, sodium gluconate	Weight loss, AC impedance, FTIR and AFM.	Mixed inhibitor, along with SG better IE was observed.	47
48	Carbon steel	Well water	Amino(trimethylene phosphonic acid) (ATMP)	Zn^{2+}, sodium tungstate	Weight loss, polarization, FTIR.	Synergistic effect found among ST, Zn^{2+} and ST. Inhibitor is Eco friendly in nature.	48
49	Mild steel	Well water	1-Hydroxyethane-1,1-diphosphonic acid (HEDP)	Zn^{2+}, sodium tungstate	Weight loss, AC impedance, polarization, FTIR.	More passivating properties offered. It works as an anodic inhibitor.	49
50	Carbon steel	Well water	*N*-(Phosphonomethyl) iminodiacetic acid (NPMIDA)	ST, Zn^{2+}	Weight loss, FTIR, polarization.	Formulation acts as a cathodic inhibitor. Better IE was found.	50
51	Carbon steel	1 M HCl	Amino(trimethylene phosphonic acid) (ATMP)		Weight loss, Electrochemical impedance spectra and Polarization studies.	It obeys Langmuir's adsorption isotherm. The mixed inhibitor	51
52	Carbon steel	1.0 M HCl	Hexamethylenediamine tetra(methylene phosphonic acid) HMDTMPA	298-328 K	Weight loss, potentiodynamic polarization, SEM, EIS.	The formulation acts as mixed inhibitor. It obeys Langmuir adsorption isotherm.	52
53	Carbon steel	0.5 M HCl	Hexamethylenediamine tetra(methylene phosphonic acid) HMDTMPA		Gravimetry and electrochemical measurements, EIS.	The mixed inhibitor nature is observed.	53

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