AN ENCOUNTER WITH CORROSION INHIBITORS

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Corrosion is a natural process. It can be defined as the destructive attack of a metal through interaction with its environment. A corrosion inhibitor is a chemical compound that, when added to a liquid or gas in small amount decreases the corrosion rate of a metal or an alloy. Corrosion inhibitors are added to coolants, fuels, hydraulic fluids, boiler water, engine oil and many other fluids used in industry. The rate of various types of corrosion inhibitors which are used in different environment to reduce the corrosion of various metals and alloys are discussed in this paper.

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Introduction

There are several methods to control corrosion. One method is modification of the environment. This can be achieved by addition of corrosion inhibitors. Corrosion inhibitors are commonly added to coolants, fuels, hydraulic fluids, boiler water, engine oil, and many other fluids used in industry. A corrosion inhibitor is a chemical compound, which when added to an environment (aqueous solution, oil, fuels and atmosphere) reduces the corrosion rate. The aim of the present paper is to provide a review on inhibitors used in various environments to reduce corrosion of various metals and alloys. Corrosion inhibition by amino acids[1] and phosphonic acids[2] has been reviewed by us recently.

Types of corrosion inhibitors

Inhibitors have been conveniently classified as Cathodic corrosion inhibitors, Anodic corrosion inhibitors, Adsorption corrosion inhibitors, Volatile corrosion inhibitors (VCI), and Mixed Inhibitors.

Cathodic corrosion inhibitors

Cathodic inhibitors reduce the corrosion rate due to retarding cathodic reactions. A cathodic inhibitor causes formation of insoluble compounds precipitating on the cathodic sites in form of a barrier film. The effective cathode area is one of the factors of galvanic corrosion. Therefore its reduction results in decrease of corrosion rate.

The following compounds are used as cathodic inhibitors: zinc salts,[3-9] calcium salts,[10-13] magnesium salts,[14,15] and polyphosphates.[16-22]

Anodic corrosion inhibitors

Anodic inhibitors reduce the corrosion rate due to retarding anodic reactions. An anodic inhibitor shifts the equilibrium of the corrosion process to the passivation zone (Pourbaix diagrams) causing formation of a thin invisible passivation oxide film on the anodic sites, which increases the anode potential and depresses the oxidation process. Reduction of the effective anode area results in decrease of corrosion rate.

Anodic inhibitors have a serious disadvantage: at low concentrations, they cause increase of corrosion rate, therefore it is important to avoid decrease of the inhibitor content below the optimum level.

The following compounds are used as anodic inhibitors: chromate (CrO_4^{2-}),[23-34] nitrite (NO_2^{2-}),[35-39] molybdate (MoO_4^{2-}),[40-46] and orthophosphate (PO_4^{3-}).[47-52]

Adsorption corrosion inhibitors

Adsorption inhibitors reduce the corrosion rate due to Polarization of the metal by extremely thin layer of their molecules adsorbed on the surface. Decrease of the effective surface area results in reduction of the corrosion rate. Adsorption inhibitors are substances (mainly organic) capable to form chemisorbed bonds with surface metal atoms.

The following compounds are used as adsorption inhibitors: amines $(R-NH_2)$,[53-58] carboxyls $(R-COOH)$,[59-62] thiourea (NH_2CSNH_2),[63-70] phosphonates $(R-PO_3H_2)$,[71-79] benzoate $(C_6H_5COO^-)$,[80-85] sulphonates.[86-93]

Table 1. Corrosion inhibitors

No.	Metal	Medium	Inhibitor	Additives	Methods	Findings	Ref
1	carbon steel	aqueous	sodium salt of diethyldithiocarbamate, 1-hydroxy ethylydene-1,1-diphosphonic acid	$ZnSO_4$	weight loss, polarization, SEM and EDS studies	NaDEDTC, HEDP and $ZnSO_4 \cdot 7H_2O$ in 1.0:1.4:1.0 ratio can decrease corrosion. System functions as both cathodic and anodic inhibitor. Protective film containing of Fe^{2+}-HEDP, Zn^{2+}-HEDP, Zn^{2+}-DEDTC complexes is formed on the metal surface.	3
2	carbon steel	low chloride environment	ascorbate	2-phosphonobutane-1,2,4-carboxylic acid and Zn^{2+}	polarisation, cathodic-impedance studies, XPS	Mixture functions as a mixed inhibitor. Immersion period of 24 h is necessary for the formation of the protective film, with a very high charge transfer resistance. The surface film consists of oxides/hydroxides of iron(III), $Zn(OH)_2$ and [Zn(II)-PBTC-ascorbate] complex.	4
3	copper	0.5 M HCl	methionine	Zn^{2+} ions	CV studies, EIS and polarization	The presence of Zn^{2+} ions increases the inhibition efficiency to 92%. The adsorption of methionine on copper surface follows Langmuir isotherm. The adsorption free energy of methionine on copper (-26 kJ mol^{-1}) reveals a strong physical adsorption of the inhibition on the copper surface.	5
4	mild steel	ground water	1-(2-pyrrole carbonyl) benzotriazole (PCBT) and 1-(2-thienylcarbonyl) benzotriazole (TCBT)	Zn^{2+} and 3-PPA	polarization, EIS, FT-IR and XRD	Characterization studies confirm the adsorption of inhibitor and the formation of corrosion products on the mild steel surface. Combination of PCBT along with Zn^{2+} and 3-PPA shows better corrosion inhibition efficiency than other inhibitor combinations and the individual inhibitors.	6
5	mild steel	sodium tripolyphosphate sodium hexametaphosphate and adenosine triphosphate	1-(2-pyrrole carbonyl) benzotriazole and 1-(2-thienylcarbonyl) benzotriazole	zinc acetate	weight loss, polarisation and SEM	Inhibition efficiency increased with increase in concentration for STPP and SHMP whereas it decreased for ATP. However, inhibition efficiency decreased for all the three phosphates with increase in temperature. All the three phosphates acted as mixed inhibitors. STPP acted through chemisorption whereas SHMP and ATP are physically adsorbed over the surface of mild steel	7
6	epoxy-coated steel		zinc phosphate	-	EIS, electrochemical noise measurement and SEM	Zinc phosphate exhibited inhibition effect on the corrosion of the scratched epoxy-coated steel. The SEM results implied that the scratched surface under zinc phosphate coating was re-healed by an insulating film.	8
7	Armco iron	3% chloride solution	piperidin-1-yl-phosphonic acid	Zn^{2+}	polarization, FTIR, weight loss method and surface analysis	Synergistic effect exists between Zn^{2+} and PPA. The film formed on iron indicates phosphonates zinc salt formation. The 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 $Zn(OH)_2$.	9
8	steel	concrete	calcium nitrite	pulverised fuel, ground granulated blast furnace slag	electrochemical assessment	Calcium nitrite was significantly effective in increasing the resistance to corrosion risk. For OPC concretes, an increase in the calcium nitrite content resulted in an increase in the time to corrosion	10
9	steel	saturated $Ca(OH)_2$	$Ca(NO_2)_2$	trisodium phosphate, calcium nitrite, 1,2,3-benzotriazole, calcium glycerol-phosphate, sodium tetraborate	open-circuit potential mapping and EIS, XPS, AFM	The passive oxide film, which is formed on the metal surface in the presence of $Ca(NO_2)_2$.	11
10	mild Steel	oxygen-containing solutions	zinc-1-hydroxyethylidene-1,1-diphosphonic acid (HEDP)	calcium and zinc	electrochemical study	The zinc-HEDP mixtures give effective inhibition at a zinc:HEDP molar ratio of 2:1 and are attributed to anodic inhibition by the 2:1 complex anion.	12
11	mild Steel	tap water	calcium gluconate	1-hydroxyethane-1,1-diphosphonic acid	weight loss, polarization and AC impedance	At higher concentrations (>50ppm), 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.	13
12	aluminium	organosilane based sol-gels	magnesium(II) nitrate	-	EIS, PDS, AFM, SEM and EDS	Superior anticorrosion properties of the Mg^{2+} rich sol-gel are due to the pore blocking mechanism of insoluble magnesium precipitates formed during the hydrolysis process.	14

Table 1. (cont.)

No.	Metal	Medium	Inhibitor	Additives	Methods	Findings	Ref
13	mild steel (C1018)	aqueous	phosphates, phosphonates, zinc and magnesium salts	anti-scaling agents	weight loss, inhibitor index	Corrosion inhibitor with the highest I.I. = 9.1 was selected and recommended for use in the cooling water system of the Oil Refinery.	15
14	carbon steel	cooling water	trisodium phosphate	Zn^{2+}	weight loss and electrochemical polarization technique	The inhibitor provides good inhibition efficiency and acts as anodic inhibitor when present alone and mixed inhibitor with zinc ions.	16
15	copper	aqueous	Na_3PO_4, $Na_5P_3O_{10}$	-	weight loss	The optimum experimental conditions maximum IE is $Na_5P_3O_{10}$, $[Na_5P_3O_{10}] = 0.017$ mol/l and passivation time tp = 2.17 h.	17
16		aqueous	polyaspartic acid	-	viscosimetry, static anti-scaling method and sha-king-bottle incubating test	The PASP has the best scale inhibition performance when its viscosity-average molecular weight is 10000 g/mol, and its inhibiting efficiency reaches over 90% to the scale of $CaCO_3$, $CaSO_4$, and $BaSO_4$ biodegradation rate can reach over 70%.	18
17	mild steel and copper	aqueous	polyphosphates and organophosphonates	CTAB, CPB	polarization studies	The inhibition efficiency towards copper was observed to be more than mild steel due to the addition of CTAB and CPB with inhibitor. Polarization studies revealed that 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.	19
18	carbon steel	aqueous	polyphosphate	sodium silicate	weight loss, EIS and polarization measurements	Silicates and polyphosphates can be useful as corrosion inhibitors for reducing the corrosion of carbon steel in potable water supply distribution systems. The optimal concentration for silicate alone was determined to be 11 ppm and for polyphosphate alone was 8 ppm. The optimum ratio of concentration for sodium silicate to sodium polyphosphate was 4:3.	20
19	steel	aqueous	condensed phosphates and polyphosphates	aluminium in a combination with zinc, strontium, calcium	weight loss	The high anticorrosion efficiency was found at a comparative pigment, represented by zinc phosphosilicate.	21
20	zinc	aqueous	zinc	polyphosphate	EIS, cyclic voltammetry	The effect of calcium to polyphosphate ratio on the corrosion rate of zinc was studied.	22
21	carbon steel	aqueous	monoethanolamine (MEA)-based compound absorbent for CO_2	piperazine (PZ) or 2-amino-2-methyl-1-propanol (AMP)	weight loss, corrosion rate	When such corrosion inhibitors were added, corrosion by MEA solution was significantly inhibited and carbon steel materials were protected effectively against corrosion, The corrosion inhibition efficiency was in the order sodium metavanadate > potassium chromate > potassium dichromate > sodium nitrite > sodium nitrate > sodium phosphate > sodium sulfite.	23
22	zinc	0.1 M NaCl	zinc chromate and zinc phosphate	-	EIS, SVET	Zinc was protected from corrosion in both extracts. SVET detected the anodic and cathodic distribution along the scribes, EIS was able to distinguish processes occurring on the metal surface exposed by the scribe in different samples. For primers with anticorrosive pigment, a time constant at high frequencies was attributed to a layer of protective nature, probably formed by metal ions from the substrate and inhibitive ions leached from the anticorrosive pigments.	24
23	duralumin alloy	acid rain solution	strontium chromate	phosphate and calcium-containing pigments	-	Nonchromate composition decreases the efficiency of cathodic processes on the intermetallic part of the model better than the chromate inhibitor due to the formation of a stable adsorption film containing zinc and aluminum phosphates.	25
24	aluminum-copper	acid medium	strontium chromate	zinc phosphate/ molybdate	surface analysis	Protective effect is caused by the deposition of a protective film on the aluminum matrix (anode) and intermetallic phase (cathode). Under the corrosion potential, a protective film, consisting of a mixture of zinc and calcium phosphates with admixture of zinc hydroxide, is formed on a specimen of the alloy.	26
25	duplex stainless steel (DSS)	LiBr media	chromate	bromide	anodic cyclic polarization curves and AC impedance measurements	The addition of halides strongly increased the inhibition efficiency of chromate. The passive film becomes more resistant when bromide concentration increases, although film thickness decreases.	27

Table 1. (cont.)

No.	Metal	Medium	Inhibitor	Additives	Methods	Findings	Ref
26	zinc	aqueous containing different amounts of chloride ions	chromate	-	FTIR, XANES and SIMS	A negative effect of the increasing chloride-to-chromate surface molar ratio on corrosion can be seen in the increasing ability to reduce oxygen on the zinc surface measured by the scanning Kelvin probe (SKP) technique. Inhibition of the cathodic reaction by chromate was less effective at higher ratios.	28
27	duplex stainless steel (DSS)	LiBr media	chromate	bromide	anodic cyclic polarization curves and AC impedance measurements.	Depending on the chromate/bromide ratio: pitting corrosion susceptibility highly decreased from a chromate/bromide ratio lower than 0.01. The comparative investigations carried out in LiBr and LiBr + 0.032 Li_2CrO_4 verify the assumption that the halide ions facilitate inhibitor adsorption. The addition of halides increased inhibition efficiency to a considerable extent. Passive film becomes more resistant when bromide concentration increases, although film thickness decreases.	29
28	steel	aqueous	chromate	1-, 2-, 3-benzotria-zole trimolybdate, tungstate	impedance tests, Frumkin-Temkin isotherm	According to the data of impedance tests and the results of evaluation of the degree of packing of these compounds on the steel surface, it is concluded that their inhibiting effect is caused by chemisorption satisfactorily described by the Frumkin-Temkin isotherm.	30
29	iron	0.1 M NaCl	zinc chromate	phosphate,	EIS, SVET and OCP measurements	Iron corroded uniformly in the phosphate extract, whereas in the chromate extract nucleation of metastable pits occurred. Evolution of the chromate layer with time was revealed, which was interpreted as being due to the formation of a porous healing layer formed on repassivated pits.	31
30	mild steel	cassava fluid	sodium chromate	diethylene amine	weight loss	The results of this study show that diethylene amine is a much better inhibitor than sodium chromate. The inhibition efficiencies by diethylene amine are higher than 85% for the 0.5, 1.0 and 1.5 M concentrations. For sodium chromate, inhibition efficiencies only become significant for 1.0 M and 1.5 M concentrations. Generally, the pH of all cassava fluid with and without inhibitors increased with duration of exposure and the corrosion rates of the mild steel decreased with increase in the pH of the cassava fluid.	32
31	mild steel	artificial acid rain solution (pH 4-5)	strontium chromate	-	polarisation, electro-chemical impedance, XPS and solution analysis	The results show that, at low concentration, strontium chromate affects the cathodic reaction, with reduction of Cr^{6+} to Cr^{3+}, and the surface film was composed of magnetite and hydrated chromium hydroxide. The presence of strontium was not found significantly to affect the inhibitory performance.	33
32	hot-dip galvanized steels		zinc coating	chromate	SKP, XPS and AES surface analysis techniques	The paper focuses on the synergetic effect of three different constituents of the chromating product: phosphates, chromates and surfactants. For this purpose two types of products have been compared, an industrial formulation (PInd) which is currently applied in the industrial lines and a reference product which has been formulated in the laboratory (PLab) in order to sort out the effect of each constituent.	34
33	mild steel	aqueous 8.6 mM NaCl solutions (pH 8)	MoO_4^{2-} or NO_2^-	-	XPS	For either anion these films are 0.5 nm deep, and the primary chemical state of iron is Fe^{3+}. Following exposure to MoO_4^{2-}, the film consists of a sub-layer (4.1 nm) composed largely of ferric oxide/hydroxide, overlaid by $Fe_2(MoO_4)_3$ (0.6 nm). As regards NO_2^-, spectra are consistent with the film being closely related to γ-Fe_2O_3. A reduction product of NO_2^-, potentially N_2 is present, displaying a depth profile comparable to that of molybdate.	35
34	mild steel	near neutral $8.6 \cdot 10^{-3}$ M (500 ppm) NaCl solution	nitrite	molybdate	polarization, weight loss, electrochemical and optical microscopy	Both nitrite and molybdate act as passivating anodic inhibitors, and they appear to have little effect on the cathodic kinetics. Various binary mixtures of these anions were also examined, and a number exhibited effective inhibition. Furthermore, two mixtures were concluded to exhibit synergistic behaviour, as regards corrosion inhibition.	36
35	steel	aqueous	nitrite	chloride	polarization method	From the results of the experiments, it was confirmed that the lithium, calcium nitrite corrosion inhibitor and new corrosion inhibitor over dosage 0.6 (NO_2^-/Cl^-) molar ratio is very effective in protecting reinforcement from corrosion in mortar in which chloride ions have contained.	37
36	steel	cement mortar	nitrites of sodium, potassium and calcium	chloride	gravimetric measure-ments, potentiodynamic polarisation studies	Potentiodynamic polarisation studies for steel in binary and ternary cement environments showed the favourable influence of the presence of higher amounts of chlorides. Nitrites of sodium, potassium and calcium act as anodic inhibitors and they compete with chloride ions for the ferrous ions at the steel to form a film of ferric oxide.	38

Table 1. (cont.)

No.	Metal	Medium	Inhibitor	Additives	Methods	Findings	Ref
37	steel	neutral and acidic solutions	nitrite	ferrous chloride and sodium chloride	gravimetrically determined weight losses, EIS	It has not been observed a significant improvement in using nitrite as inhibiting agent in these systems. The corrosion seems to be related to the $[Cl^-]/[OH^-]$ ratio in three different regions of pH identified from acid to alkaline pH values.	39
38	steel	5% NaCl saturated $Ca(OH)_2$ solution	sodium molybdate	NaCl	polarization, EIS and Mott-Schottky analysis technique	The inhibition behavior of sodium molybdate is due to the stability of film on the metal surface through the competitive adsorption with Cl^-. Mott-Schottky (M-S) measurements confirmed the passive film formed on steel rebar surface was an n-type semi-conductor. Moreover, with increasing concentration of inhibitor, the passive film was more compact and stable than that in the absence of inhibitor.	40
39	hot-dip galvanized steels	aqueous	molybdate	silane	SEM, XPS, AES, and RAIR	The results showed that the molybdate/silane composite film formed in the single-step process had a similar double-layer structure as that obtained in the two-step process. For the film corrosion current was reduced, the impedance and the corrosion resistance were increased.	41
40	Q235 steel	5 g/L Cl^- solution	molybdate	silicate, phosphate and organic amine A	EIS, weight loss	Molybdate can reach better inhibition effect by compounding with silicate, phosphate and organic amine A. Corrosion inhibition efficiency of the compound inhibitors is near 84. 4%, which is better than any individual inhibitor studied.	42
41	carbon steel	0.5 M NaCl solution	molybdate	chromate	AFM, polarization, EIS	Both CrO_4^{2-} and MoO_4^{2-} have inhibition effect on carbon steel corrosion, and the inhibition efficiency increases with increase in concentrations of CrO_4^{2-} and MoO_4^{2-} at the same concentration, the inhibition efficiency of CrO_4^{2-} is higher than that of MoO_4^{2-}. The increase in concentrations of CrO_4^{2-} and MoO_4^{2-} anions causes a shift of the breakdown potential (E_b) in the positive direction, indicating the inhibitive effect of the added anions on the pitting attack AFM force-distance curves indicate that the passive film of CrO_4^{2-} is much stiffer than that of MoO_4^{2-}.	43
42	cold rolled steel (CRS)	peracetic acid (PAA) solution	sodium molybdate	-	gravimetric measurements, polarization curves, EIS	Na_2MoO_4 acts as a very good inhibitor in PAA solution. The inhibition efficiency increases with increasing concentration of Na_2MoO_4 and immersion time. The inhibition efficiencies, calculated from the three techniques are in reasonably good agreement and are very similar in the three cases. Na_2MoO_4 behaves as an anodic passive type inhibitor.	44
43	mild steel	LiBr-ethylene glyol soln.	lithium molybdate	-	rescale range analysis (R/S), EIS	The fractal analysis of electrochemical noise helps to evaluate the inhibitor protection performance under the tested corrosion conditions.	45
44	bronze	0.5 mol/L NaCl solution	sodium molybdate	benzotriazole (BTA)	polarization, EIS, XPS	The results show that combined action of BTA and sodium molybdate had a good synergistic effect of corrosion inhibition. They increased the resistance of anodic polarization of bronze. A polymer protective layer is formed on the bronze surface. The surface layer was consisted of [Cu (I) BTA] polymer film with deposit of SnO_2, PbO, MoO_3. It shows a good compactness and a good protection from chloride iron.	46
45	lead	chlorinated water	orthophosphate	-	SEM, TEM, XRD, and XANES analysis	In the absence of orthophosphate (DIC = 10 mg C/L, 24 °C, pH 7.75-8.1, 3 mg Cl_2/L goal), Pb(IV) oxides formed with time following a transformation from the Pb(II) mineral hydrocerussite. Orthophosphate dosing inhibited the formation of Pb(IV) oxides. The Pb(II) mineral hydroxypyromorphite, $Pb_5(PO_4)_3OH$, was the only mineral phase identified during the entire study of over 600 days, although the presence of some chloropyromorphite, $Pb_5(PO_4)_3Cl$, could not be ruled out. The findings provide an important explanation for the absence of Pb(IV) oxides in some water systems that have used, or currently use,	47
46	copper	aqueous	phosphate	-	using standardised on-site corrosion tests	Phosphate dosing decreased the copper oxidation and resulted in lower copper concentration in water. Likewise phosphate hindered the precipitation of cupric ions, which prolonged the existence of copper in water and resulted in a higher copper concentration.	48
47	copper	aqueous	orthophosphate	sodium alginate and fulvic acid	weight loss	Effect of stagnation time on soluble copper release from different aged copper pipe in soft water was highly variable. Compared to the system of no organic matters, organic matters markedly decreased the efficiency of orthophosphate corrosion inhibition for copper pipe in soft water.	49
48	mild steel	phosphoric acid	phosphate of aluminum	-	weight-loss, potentiodynamic polarisation and EIS measurements	Polarization studies show that PA is a mixed-type inhibitor and acts both on the cathodic and anodic reactions without changing the mechanism of the hydrogen evolution reaction. PA adsorbs on the steel surface according to a Langmuir isotherm adsorption model.	50

Table 1. (cont.)

No.	Metal	Medium	Inhibitor	Additives	Methods	Findings	Ref
49	copper	aqueous	polyphosphate	-		Moderate doses of polyphosphate or orthophosphate generally decreased copper release whereas higher doses of orthophosphate tend to decrease copper solubility.	51
50	copper	aqueous	orthophosphate	hydroxyl binder groups		The highest anticorrosion efficiency is reached with pigments which are modified by organic corrosion inhibitors. The highly water soluble phosphate pigments reduce the anticorrosion coating properties. The effect of cation in phosphate pigments on the corrosion inhibition was confirmed.	52
51	silver	dilute nitric acid (0.01M)	methylamine, ethylamine, n-propylamine, and n-butylamine	-	electrochemical polarization technique, Tafel plots	Inhibition efficiency obtained from Tafel plots improved when the inhibitor concentration and the length of the alkyl chain.	53
52	steel	saturated NaCl solution	amine-alcohol	-	EIS, polarisation	The surface of the electrode changes from passive state to active state. The best inhibition was obtained in the presence of the CI inhibitor.	54
53	aluminium	1.0 M HNO$_3$	thiosemicarbazone derivatives	-	polarization curves, EIS with quantum chemical calculations and molecular dynamics simulations	he thiosemicarbazone derivatives were of mixed-type inhibitors. EIS plots indicated that the addition of thiosemicarbazone derivatives increases the charge-transfer resistance of the corrosion process, and hence the inhibition performance. The molecular dynamics simulation results show that the three thiosemicarbazone derivatives can adsorb on the A_2O_3 (111) surface through the sulphur and nitrogen atoms as well as π-electrons in the pyridyl structure.	55
54	copper	acid	methyl amine, dimethyl amine, diethyl amine, triethyl amine, diethanol amine, and triethanol amine	-	anode limiting current, Langmuir, Flory-Huggins, and kinetic adsorption isotherms	It is suggested that the decrease in the rate of corrosion is attributed to the increase in interfacial viscosity of the solution and decrease the diffusion coefficient of the copper ion. It has been found that the rate of inhibition is increases in order: methyl amine, dimethyl amine, diethyl amine, triethyl amine, diethanol amine, and triethanol amine.	56
55	mild steel	1M HCl	N, N'-dibensylideneethane-1,2-diamine (baen)	chloro, methyl, and hydroxyl substituents	polarisation method	The presence of chloro, methyl and hydroxyl substituents enhance the inhibitive properties of N, N'-dibensylideneethane-1, 2-diamine. Cbaen achieved the highest inhibition efficiency of 80.76% at $1 \cdot 10^{-3}$ M.	57
56	iron	1M HCl	poly(p-phenylene diamine)	-	polarization techniques and electrochemical impedance spectroscopy	Poly(p-phenylene diamine) was a more efficient corrosion inhibitor than the monomer and gave an 85% inhibition efficiency at a concentration of 50 ppm, whereas the monomer gave an efficiency of 73% at 5000 ppm.	58
57	carbon steel	cooling water	sodium octanoate	-	potentiodynamic polarization and weight loss, FTIR	Results revealed that the concentration should not fall below 200 ppm for the tested inhibitor to be effective. The adsorption of inhibitor on the carbon steel surface was found to obey the Langmuir adsorption isotherm model. FTIR spectra revealed that octanoate was adsorbed on the steel surface via its functional group.	59
58	mild steel	cooling water	dextran containing carboxyl groups	-	weight loss	The Inhibitor showed moderate corrosion inhibition activity for mild steel, and biodegradability under conditions for cooling water systems.	60
59	carbon steel	aqueous	polyepoxysuccinic acid (PESA)	Zn^{2+}, sodium gluconate	weight loss	The synergistic effect exists among PESA, Zn^{2+} and sodium gluconate and the corrosion inhibition efficiency for carbon steel is higher than 99%.	61
60	carbon steel	river water	calcium propionate	Zn^{2+}	mass-loss, polarization, FTIR spectra	The system controls cathodic reaction predominantly. Protective film is formed on the metal surface. Protective film consists of Fe^{2+} - CP complex Zn(OH)$_2$ and Ca(OH)$_2$.	62
61	stainless steel	3M hydrochloric acid	N-cyclohexyl-N'-phenyl thiourea (CPTU)		polarization technique, SEM	The thermodynamic parameters of adsorption deduced revealed a strong interaction and spontaneous adsorption of CPTU on the steel surface. Scanning electron microscopic study (SEM) was done to investigate the surface characterization of inhibited and uninhibited 304 SS specimens.	63
62	carbon steel	CO$_2$-saturated 3 wt.% NaCl solution	2-undecyl-1-sodium ethanoate-imidazoline salt (2M2)	thiourea (TU)	electrochemical methods, Langmuir adsorption isotherm	Inhibition efficiency increased with increase in 2M2 concentration but decreased with increase in TU concentration with optimum. The data suggest that the compounds functioned via a mixed-inhibitor mechanism. A synergistic effect was observed between TU and 2M2.	64
63	iron	1.0 M solution of HNO$_3$	N-methyl thiourea (MTU), N-propyl thiourea (PTU), and N-allyl thiourea (ATU)	-	weight loss, Tafel polarization and electrochemical impedance spectroscopy, EIS	These compounds revealed a good corrosion inhibition, (ATU) being the most efficient and (MTU) the least. The efficiency order of the inhibitors obtained by experimental results was verified by theoretical analysis.	65

Table 1. (cont.)

No.	Metal	Medium	Inhibitor	Additives	Methods	Findings	Ref
64	mild steel	0.5 M H_2SO_4	acetyl thiourea chitosan polymer (ATUCS)	-	polarization, EIS, SEM	EIS showed that the resistance (R_{ct}) increases slightly with increasing immersion time indicating a slight decrease in corrosion rate of the steel with time. Also, the corrosion rate increases with either increasing temperature or decreasing the polymer concentration. ATUCS has shown very good inhibition efficiency (IE) in 0.5 M sulphuric acid solution reaches to 94.5% for 0.76 mM concentration. IE of this compound has been found to vary with the concentration of the polymer solution, immersion time and temperature.	66
65	ingot iron	dilute HCl solution	allyl-thiourea (ATU)		potentiodynamic polarization tests	The phenomenon of desorption appears at the concentration of 100 mg/L, but the variation of the potential E_{des} between us is obvious. The inhibition effect of ATU for BNII is limited by comparison with CPII.	67
66	stainless steel	0.5 M H_2SO_4 solution	1-methyl-3-pyridine-2-yl-thiourea (MPT)	-	weight loss and polarization	MPT is of the mixed-type inhibitor. The adsorption of this inhibitor is also found to obey the Langmuir adsorption isotherm. Scanning electron microscopy indicated uniform film on the surface.	68
67	stainless steel	acid	0.004-0.007 M of 1-methyl-3-pyridine-2-yl-thiourea (MPT)	-	potentiostatic polarization measurements.	Corrosion potential (E_{corr}) increases with increasing MPT concentrations, while corrosion current (i_{corr}) decreases. Inhibition efficiency of MPT is slightly more in 1 M H_2SO_4 than in 1 M HCl. The inhibitor functions through adsorption and follows Temkin isotherm in both the acids. Activation energy (E_a) and Gibbs free energy (E_a) for adsorption of MPT are calculated. The values of G_{ads} decreased (attained more negative values) with increasing temperature.	69
68	mild steel	H_2SO_4 solution	1-methyl-3-pyridin-2-yl-thiourea	-	different techniques.	Inhibition efficiency increases with the increase of inhibitor concentration. This compound affects both the anodic dissolution of steel and the hydrogen evolution reaction in 0.5 M H_2SO_4. The adsorption of this inhibitor is also found to obey the Langmuir adsorption isotherm.	70
69	ordinary steel	aqueous	phosphonate anion (PHOS)	cetyltrimethyl-ammonium bromide (CTAB)	weight loss, polarization curves, EIS	PHOS perform excellently as corrosion inhibitor for ordinary steel in simulated cooling water. The inhibition efficiency of PHOS was increased with increasing both its concentration and water circulation velocity. 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.	71
70	carbon steel	low chloride aqueous medium	tungstate	N,N-bis(phosphonomethyl) glycine (BPMG) and zinc ions	polarisation studies, impedance studies, XPS reflection absorption FTIR	The synergistic action of tungstate has been established through the present studies. System functions as a mixed inhibitor. The surface film is highly protective and it consists of iron, phosphorus, nitrogen, oxygen, carbon, zinc and tungsten in the surface film.	72
71	carbon steel	low chloride environment	2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC)	ascorbate, Zn^{2+}	Polarisation, impedance studies, XPS, FTIR	The synergistic effect of ascorbate has been established from the present studies. In the presence of ascorbate, lower concentrations of PBTC and Zn^{2+} are sufficient in order to obtain good inhibition. This mixture functions as a mixed inhibitor, predominantly cathodic. An immersion period of 24 h is necessary for the formation of the protective film, with a very high charge transfer resistance. The film is stable even at 60 °C in the presence of the inhibitor in the corrosive environment.	73
72	carbon steel	1 M HCl solution	aminotris-(methylenephos-phonic) acid (ATMP)	-	weight loss, polarization, EIS techniques, Tafel polarization	The inhibition efficiency increased with increasing inhibitor concentration. ATMP acts as a mixed inhibitor. It obeyed the Langmuir adsorption isotherm. Corrosion inhibition o is mainly controlled by a physisorption process. ATMP have an antibacterial effect against both Gram positive and Gram negative bacteria. The MIC of ATMP against Listeria innocua in a buffered medium (pH 6.5) was of ca. 4-fold higher than MIC measured in unbuffered medium. The antibacterial activity of ATMP is a result of a combined effect of the pH solution and the chemical nature of the used phosphonate.	74
73	carbon steel	aqueous soln. containing 60 ppm of Cl⁻	diethylenetriaminepenta-methylenephosphonic acid	zinc, sodium gluconate	weight loss, EIS, FTIR, AFM	System functions as a mixed inhibitor. A protective film is formed on the metal surface. It consists of Fe^{2+}-DTPMP complex, Fe^{2+}-SG complex and $Zn(OH)_2$.	75
74	high purity polycrystalline zinc	aqueous	1,5-diphosphono-pentane (DPP) and 1,7-diphosphono-heptane (DPH)	-	XRD and XPS, GD-OES	The corrosion inhibition was explained by the formation of insoluble zinc-phosphonate salt on the zinc surface, blocking the zinc dissolution process.	76

Table 1. (cont.)

No.	Metal	Medium	Inhibitor	Additives	Methods	Findings	Ref
75	mild steel	aqueous	1-hydroxyethylidene 1,1 diphosphonic acid (HEDP)	sodium silicate	EIS, Tafel polarization techniques, polarization, SEM	Inhibitors mixtures have shown synergistic effects at lower value of HEDP. The surface homogenity increases in case of inhibitors mixture application and this provides good protection to mild steel against corrosion in soft water solution.	77
76	steel	1 M HCl	sodium methyl dodecyl phosphonate and sodium methyl (11-methacryloyl-oxyundecyl) phosphonate	-	EIS, polarisation, weight loss measurements	The dissolution process of steel occurred under activation control. The inhibitors tested acted as cathodic inhibitors.	78
77	mild steel	well water	sodium tungstate	Zn^{2+}, HEDP	weight loss, A.C impedance, polarization	The system works as an anodic inhibitor. Charge transfer resistance increases, double layer capacitance decreases. Hence a protective film is formed on the surface.	79
78	steel	alkaline solution	sodium tartrate, sodium benzoate, sodium glutamate, DMEA and TETA	-	EIS and potentiodynamic tests	Theoretical calculations based on molecular mechanics and molecular dynamics were used to establish which functional groups bind to the passive film, the strength of their binding, the functional groups contributing to their filming, and their evolution with time.	80
79	carbon steel	30 mg l^{-1} NaCl + 70 mg l^{-1} Na$_2$SO$_4$ aq. solution	sodium benzoate	-	polarization curves, EIS	Corrosion inhibition of sodium benzoate in near-neutral aqueous solution was increased as the grain size of iron was decreased from microto nanocrystalline surface.	81
80	iron	30 mg L^{-1} NaCl + 70 mg L^{-1} Na$_2$SO$_4$	sodium benzoate	-	Tafel polarization curves, EIS	Results obtained suggested that the inhibition effect and corrosion protection of sodium benzoate inhibitor in near-neutral aqueous solutions increased as the grain size decreased from microcrystalline to nanocrystalline. The improvement on the inhibition effect is attributed to the increase of the surface energy.	82
81	steel	alkaline solution	sodium tartrate, sodium benzoate, sodium glutamate, dimethylethanolamine and triethylenetetramine	-	EIS, potentiodynamic tests	The theoretical results showed the presence of favourable interaction energy with the surface of the adsorbed molecules, with repulsive intermolecular interactions, mainly among the anions. The adsorption isotherms confirmed both the presence of a strong physisorption between the inhibitors and the substrate, and of repulsive interactions between the molecules of inhibitors, leading to the formation of a non-homogenous monolayer.	83
82	carbon steel	aqueous	sodium benzoate and sodium-(phenylamino) benzenesulfonate	-	gravimetric method, FTIR	These inhibitors retard the anodic dissolution of low carbon steel by protective layer bonding on the metal surface.	84
83	stainless steel	seawater	sodium benzoate	-	weight loss	The highest corrosion rate is observed for the stainless steel with no inhibitor was added to the seawater. As the concentration of sodium benzoate being increased, the corrosion rate is decreases. Results show that by the addition of 1.0M of sodium benzoate in seawater samples, it giving ≥ 90% efficiencies	85
84	mild steel	sulphuric acid solution	sodium dodecyl benzene sulphonate	hexamethyle-netetramine	weight loss, electrochemical impedance and Tafel polarisation measurements	For HA, a monotonous increase in inhibition efficiency is observed as a function of concentration. For SDBS, however, an optimum in the inhibition efficiency is observed for a concentration close to 250 ppm. Upon mixing HA and SDBS, concentration regions showing synergistic and antagonistic inhibition behaviour are identified, and it is concluded that electrostatic interactions between adsorbate ions are likely responsible for both phenomena.	86
85	mild steel	0.5 M H$_2$SO$_4$ solution	p-toluene sulphonic acid doped copolymer	-	weight loss, polarization and electrochemical impedance techniques	The inhibition efficiency has been found to increase with increase in inhibitor concentration, solution temperature and immersion time. A strong interaction between inhibitor and mild steel surface. The adsorption of this inhibitor on the mild steel surface obeyed the Langmuir adsorption equation.	87
86	Armco iron	0.5 mol dm^{-3} H$_2$SO$_4$ solution	naphthalenesulfonic acid, 2,7-naphthalenedisulfonic acid and 2-naphthol-3,6-disulfonic acid	-	weight loss, polarization	The inhibitors behave as a cathodic corrosion inhibitors. The inhibitive efficiency, changes with the number of functional groups substituted on benzene ring and increases with concentration.	88
87	aluminium	hydrochloric acid solution	dodecyl sulphonic acid sodium salt, dodecyl benzene sulfonic acid sodium salt and sodium dodecyl sulfate	-	weight loss method	The adsorption of the inhibitor could prevent aluminium from weight loss and the adsorption was according to Langmuir equation. Thermodynamic parameters such as adsorption heat, adsorption free energy were calculated.	89

Table 1. (cont.)

No.	Metal	Medium	Inhibitor	Additives	Methods	Findings	Ref
88	stainless steel, nickel alloys, and refractory metals	methane sulphonic acid		ferric and nitrate ions	weight loss coupon exposure tests and potentiodynamic polarisation measurements	It was found that most of the stainless steels, nickel alloys, and titanium corrode to a considerable extent, whereas Hastelloy G-30, zirconium, and tantalum withstand this environment. The addition of ferric and nitrate ions was found to produce an inhibiting effect.	90
89	steel	cooling water systems	copolymer of acrylic acid-diphenyl amine sulphonic acid	-	constant potential electrolysis, EIS, SEM XRD	AA-DPSA polymer acts as a very good antiscaling inhibitor both in the carbonate and sulphate brines. Copolymer of acrylic acid-diphenyl amine sulphonic acid can be used safely in cooling water industries.	91
90	mild steel	-	poly(styrene sulphonic acid)-doped polyaniline	-	weight loss galvanostatic polarisation studies, electropermeation studies and a.c. impedance	The polymer acts predominantly as an anodic inhibitor and corrosion inhibitor. The adsorption of the compound on the mild steel surface obeys Temkin's adsorption isotherm.	92
91	stainless steel	3% NaCl solution	poly(o-anisidine)-dodecyl-benzenesulfonate)	-	OCP, polarization technique, EIS	POA-DBSA acts as a corrosion protective coating on steel and reduces the corrosion rate (CR) of steel almost by a factor of 14.5.	93
92	mild steel	HCl	bipyrazolic derivatives	-	functional approach B3LYP/6-31G(d) calculations	The bipyrazole inhibitors exhibited the highest inhibition efficiency. The quantum chemical parameters calculated are, the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), the gap energy (ΔE), the dipole moment (μ), the softness (σ) and the total energy (TE).	94
93	steel	2 wt.% NaCl and 1 wt.% Na_2SO_4	dicyclohexylamine nitrite or sodium dihydrogen ortho phosphate	-	weight loss	Treatment of steel with either dicyclohexylamine nitrite or sodium dihydrogen orthophosphate both at 10 mM concentration for 1 day at room temperature resulted in significant inhibition of corrosion.	95
94	copper	3% NaCl solution	(bipy1); (bipy2); (bipy3); (bipy4); (bipy5); (bipy6)	-	cathodic Tafel plots, polarisation resistance weight loss, EIS	The studied molecules act as mixed-type inhibitors. Detailed study of bipy1 shows that the maximum inhibition efficiency revolves around 99 per cent from $5 \cdot 10^{-4}$ M of inhibitor. This latter adsorbs on the copper surface according to the Frumkin isotherm model. The inhibition efficiency of bipy1 decreases with the rise of temperature in the range 25 - 60°C.	96
95	carbon steel	2.0% NaCl and 1.0% Na_2SO_4	sodium dihydrogen ortho phosphate, dicyclohexylamine nitrite and sodium benzoate	-	electrochemical methods	Sodium dihydrogen orthophosphate had the best performance among the three inhibitors. It was still effective at the end of 180 days of atmospheric exposure. The performances of dicyclo-hexylamine nitrite and sodium benzoate, on the other hand, were effective in the early stages of the atmospheric exposure. Their inhibition effectiveness deteriorated with further exposure to the atmosphere, being totally ineffective by the end of the exposure period.	97
96	carbon steel		dicyclohexylamine, dicyclohexylamine nitrite	-	polarization and the electrochemical impedance methods	The corrosion rate decreased significantly in the acid vapours at high humidity when a volatile corrosion inhibitor was also present.	98
97	coupled steel trod zinc	aqueous	dicyclohexylamine nitrite	-	mass loss, polarisation and ac impedance measurements	DCHN acts as an anodic inhibitor in the corrosion of mild steel. For zinc, DCHN acts to accelerate corrosion. This is attributed to surface chelation between DCHN and zinc, resulting in the formation of a soluble complex.	99
98	copper	0.5 M sulphuric acid	N-(5,6-diphenyl-4,5-dihydro-[1,2,4] triazin-3-yl)-guanidine	-	weight loss, polarization, EIS	NTG is a cathodic-type inhibitor for copper in 0.5 M H_2SO_4 solutions. Adsorption of NTG on the surface of copper is found to obey the Langmuir adsorption isotherm.	100
99	copper	neutral solution of 3% NaCl	N-(5,6-diphenyl-4,5- dihydro-[1,2,4]triazin-3-yl)guanidine	-	weight loss polarization, EIS, EFM	These studies have shown that NTG was a very good inhibitor and the inhibition efficiency up to 99% in 3% NaCl is obtained. The adsorption of the inhibitor on the copper surface in the acid solution was found to obey Langmuir's adsorption isotherm.	101
100	Armco iron	molar hydrochloric acid (1 M HCl)	polyphosphate derivative of guanidine and urea copolymer	-	EIS	PGUC is an efficient inhibitor and the inhibition efficiency increases with increase in inhibitor concentration. This inhibitor can be used as biocides in aqueous environment. PGUC has a broad inhibitory spectrum against both Gram positive and Gram negative bacteria.	102

Volatile corrosion inhibitors (VCI)

Volatile corrosion inhibitors (VCI) reduce corrosion in closed spaces (package bags), VCI compound is emitted (vaporized) by the material enclosing the space. The vapours condense on the metal surface in form of microscopic crystals, which dissolve in the moisture film present on the surface. The ions of the dissolved VCI displace water molecules from the metal surface and form monomolecular invisible protection film reducing the corrosion rate. Volatile corrosion inhibitors may be added to various package materials: polymer film (e.g. low density polyethylene), paper, foam, powder, oils, etc.). The following compounds are used as Volatile corrosion inhibitor*s* (VCI): cyclohexylamine,[94-96] dicyclohexyl-amine,[97-99] guanidine.[100-102]

The choice of inhibitors very much depends on the metal to be protected and the medium with which metal is in contact. The results are summarized in Table 1.

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