



# INHIBITORS FOR PREVENTION OF CORROSION OF METALS IN SEA WATER – AN OVERVIEW

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An accepted practice is the use of inhibitors in the corrosion control of metals and its alloys which are in contact with any aggressive medium such as sea water. Inorganic and organic compounds have been studied for their corrosion control potential; these studies reveal that the inhibitors especially with the polar atoms such as P, N, S and O showed excellent inhibition efficiency (IE). The inhibitors adsorbed on the metal surface through the polar atoms; protective films are formed. The protective films have been analyzed by surface characterization studies such as UV, fluorescence spectra, FTIR, SEM, EDX, Raman spectroscopy, Auger electron spectroscopy, XRD, XPS and AFM. Adsorption of the inhibitors obeys various adsorption isotherms. The IE has been investigated by electrochemical studies such as polarization, impedance spectroscopy, open circuit potential and cyclic voltammetry, etc. The conclusion of this article gives vivid account of both inorganic and organic compounds which are used as corrosion inhibitors for various metals and its alloys in natural/artificial sea water medium.

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## Introduction

Corrosion is a natural, spontaneous and thermodynamically favourable process. It can be controlled, but it cannot be prevented completely. It means corrosion mitigation and control methods shall be properly selected to meet the specific environment and operational condition. Depending upon the metal/environment combinations, different types of inhibitors are used in suitable concentrations. The use of inhibitors is an important method of protecting materials against corrosion.

Sea water is the well known aggressive medium containing high chloride ions causing severe corrosion problems. Various inorganic and organic compounds have been tried and reported as inhibitors for metals and its alloys in neutral chloride medium. The inhibitors contain heteroatoms such as P, N, S and O coordinate with the corroding metal ions, through their electrons and hence protective films are formed on the metal surface so that corrosion is prevented.<sup>1-116</sup>

## Inhibitors

Both inorganic compounds<sup>14, 16, 17, 21, 24, 32, 38, 55, 60, 63, 74, 76, 80, 81, 95, 100, 101, 110</sup>, and organic compounds – naturally available<sup>5, 22, 62, 88, 89, 113, 116</sup> and synthesized compounds<sup>1-4, 6-13, 15, 18-20, 23, 25-31, 33-37, 39-54, 56-59, 61, 64-73, 75, 77-79, 82-87, 90-94, 96-99, 102-109, 111, 112, 114, 115</sup> have been used to control the corrosion of various metals and its alloys in natural/artificial sea water medium.

## Metals

The inhibitors have been used to control the corrosion of various metals such as Fe,<sup>12, 18, 24, 27, 38, 71, 73, 98, 100</sup> carbon steel,<sup>2, 3, 5, 8, 13, 15, 23, 32, 40-43, 54, 55, 58, 62, 63, 67, 70, 74-76, 86, 96, 99, 110, 112, 113, 115</sup> mild steel,<sup>1, 4, 35, 44, 45, 57, 61, 72, 106</sup> stainless steel<sup>79, 80, 83, 85</sup>, Al and its alloys,<sup>9, 10, 14, 16, 21, 37, 56, 60, 66, 69, 95, 101, 103, 107, 111</sup> Zn and its alloys,<sup>17, 77</sup> Cu and its alloys<sup>6, 7, 11, 19, 20, 22, 24-26, 28-30, 33, 34, 36, 39, 46-53, 59, 64, 65, 68, 73, 78, 81, 82, 84, 87-94, 97, 102, 104, 105, 108, 109, 114, 116</sup> and Ni and its alloys<sup>24, 31</sup> in natural/artificial sea water medium.

## Medium

The inhibition efficiency (IE) of various inhibitors, in controlling corrosion of metals and its alloys in natural sea water medium<sup>1, 2, 5, 6, 21, 27, 34, 35, 62, 67, 69, 70, 77, 80, 81, 88-90, 101, 103, 104</sup> and artificial sea water medium<sup>3, 4, 7-20, 22-33, 36-61, 63-66, 68, 71-76, 78, 79, 82-87, 91-100, 102, 105-116</sup> have been studied.

## Additives

Along with the inhibitors, substances like EDTA<sup>1</sup>, Al<sup>3+</sup> and Mg<sup>2+</sup><sup>3</sup>, Ca<sup>2+</sup><sup>3, 42</sup>, Zn<sup>2+</sup><sup>4, 13, 15, 23, 58, 71, 72</sup>, thiosulphate<sup>8</sup>, docosanol<sup>34</sup>, KI<sup>41</sup>, sodium benzoate<sup>44</sup>, oxalic acid<sup>45</sup>, sulphides<sup>51</sup>, carbon black<sup>54</sup>, Ni<sup>2+</sup><sup>58</sup>, cysteine<sup>109</sup> and SiO<sub>2</sub><sup>110</sup> have been used to enhance the corrosion inhibition process. Moreover, ammonia,<sup>26, 105</sup> ethanol,<sup>28, 53, 75, 88</sup> dilute NaOH,<sup>32</sup> toluene<sup>53</sup> and acetic acid<sup>63</sup> have been employed as solvent for the dissolution of inhibitors.

## Temperature

The IE of various inhibitors have been evaluated at room temperature,<sup>1-38, 40, 41, 43-62, 64-71, 73-87, 89-98, 100-116</sup> and also at higher temperatures<sup>39, 42, 63, 72, 81, 88, 95, 99</sup>.

Table 1. Corrosion inhibitors for seawater

| S.No. | Metal                 | Medium   | Inhibitor   | Additive                              | Method  | Findings   | Ref |
|-------|-----------------------|--|---|---------------------------------------|---|--|-----|
| 1     | Mild steel            | Sea water (Dona Paula Bay, Arabian Sea)                          | Exopolysaccharide (EPS)   | 10-mM EDTA, 2N HCl                    | Weight loss, capillary gas chromatography and growth curve experiments.                                       | EPS is a strong corrosion inhibitor, protective film consists of metal-polysaccharide complex and EPS served as a structural matrix polymer.   | 1   |
| 2     | Carbon steel          | Sea water  | Non-ionic polyoxy-ethylene monopalmitate (PaEO), cationic hexadecyltrimethylammonium bromide (HTABr) and anionic sodium dodecyl-sulphate (SDS).   |                                       | Weight loss study and X-ray diffraction analysis.   | IE increases with inhibitor concentration, obeys Langmuir isotherm and the order of inhibition is $SDS < HTABr < PaEO$ .   | 2   |
| 3     | Steel                 | 3.5% NaCl and sea water  | Thiourea (TU)   | $Al^{3+}$ , $Ca^{2+}$ and $Mg^{2+}$ . | Potentiodynamic polarization study.   | Cathodic inhibitor, IE in presence of $Al^{3+}$ ion is about 90% and interpretation of corrosion inhibition mechanism and cathodic control.  | 3   |
| 4     | Mild steel            | Chloride medium  | 2-carboxyethyl phosphonic acid (CEPA) and ethyl phosphonic acid (EPA)   | $Zn^{2+}$                             | Polarization study and fluorescence spectra.  | Mixed-type inhibitor, IE decreases as the immersion period increases and IE of CEPA is better than CPA.  | 4   |
| 5     | Carbon steel          | High saline water  | Natural honey (NH)  |                                       | Weight loss and potentiostatic polarization technique.  | IE increases with inhibitor concentration, but decreases due to the growth of fungi and obeys Langmuir adsorption isotherm.  | 5   |
| 6     | CuNi <sub>10</sub> Fe | Sea water  | Sodium-diethyl-dithiocarbamate (NaDDTC)   |                                       | Weight loss, polarization measurements, EIS and Auger electron spectroscopy (AES) studies.                    | Mixed-type inhibitor and the inhibition film do not lose efficiency even at anodic polarization.   | 6   |
| 7     | Cu                    | Aerated 3% NaCl solution   | 2-mercapto-1-methylimidazole (McMIm)  |                                       | Electrochemical polarization, impedance spectra, cyclic voltammetry and IR spectra techniques.                | Mixed-type inhibitor, excellent inhibitor for Cu corrosion and IE from cathodic Tafel plots and polarization were in good agreement.   | 7   |
| 8     | Carbon steel          | 5% NaCl + 0.5% acetic acid                                       | n-dodecylquinolinium bromide (DDQB), n-dodecylpyridinium chloride (DDPC), benzyl-stearyl-dimethylammonium chloride (BSDMAC), 1-(2-aminoethyl)-2-n-tridecyl-3-imidazole (IMI-13), 2-n-hexyl-3-imidazole (IMI-6), 2-n-tridecyl-3-imidazole (IMI) and N-phenyl-ennamylideneamine (PH-ATC). | $S_2O_3^{2-}$                         | Weight loss and polarization studies.   | IE of the inhibitor ranging between 74 and 96% and IE of DDQB, DDPC and IMI were almost same.  | 8   |
| 9     | Al – Brass            | 3.5% NaCl solution and sea water                                 | Anionic sodium dodecylbenzene sulphonate (SDBS), nonionic dodecyl phenol ethoxylated with 9 units of ethyleneoxide (DPh(EO) <sub>9</sub> ) and cationic 1,1-laurylamidopropyl ammonium chloride (LAPACI)  |                                       | Potentiodynamic polarization and cyclic voltammetric studies.   | IE increases with inhibitors concentration and the order of inhibition is $SDBS > LAPACI > DPh(EO)_9$  | 9   |
| 10    | Arsenical Al brass    | 3.5% NaCl solution   | 1,2,4,5 tetraza spiro (5,4) decane-3 thione   |                                       | Weight loss, potentiodynamic polarization and impedance measurements, UV, XRD and SEM studies.                | Mixed-type inhibitor and obeys Langmuir adsorption isotherm.   | 10  |
| 11    | Brass                 | 3% NaCl and artificial sea water                                 | Benzotriazole (BTA), gluconic acid sodium salt (GASS) and polyphosphonic acid sodium salt (PP)  |                                       | Electrochemical impedance spectroscopy (EIS) and electrochemical noise analysis (ENA).                        | BTA shows excellent corrosion inhibition in both media than the others, PP is not shows effective inhibition and GASS shows maximum inhibition at the concentration of 0.01 M.   | 11  |
| 12    | Fe                    | 3.0 mol / L NaCl solution saturated with 0.1 MPa CO <sub>2</sub> | Imidazole amide (IM)  |                                       | Electrochemical impedance spectrum, polarization curves, scanning tunneling microscopy (STM) and XPS studies. | Obeys Langmuir adsorption isotherm and thermodynamic theory, $\Delta G^{\circ} = 30.4 \text{ kJ / mol}$ , pendant functional group of IM plays key role in the inhibition and the increase of temperature and chloride ion decreases the adsorption potential. | 12  |
| 13    | Carbon steel          | Neutral aqueous environment containing 60 ppm Cl <sup>-</sup>    | Carboxymethyl phosphonic acid (CMPA) and 2-carboxyethyl phosphonic acid (2-CEPA)  | $Zn^{2+}$                             | Weight loss, XRD, FTIR and luminescence spectral studies.   | Mixed-type inhibitors, synergistic effect, IE of CEPA better than CMPA and the protective film consists of $Fe^{2+}$ -phosphonate complex and $Zn(OH)_2$ .   | 13  |

Table 1 (cont.). Corrosion inhibitors for seawater

| S.No. | Metal              | Medium                                  | Inhibitor  | Additive         | Method  | Findings  | Ref |
|-------|--------------------|---|--|------------------|---|---|-----|
| 14    | AA5083 Al-Mg alloy | 3.5% NaCl solutions                     | CeCl <sub>3</sub> and LaCl <sub>3</sub>  |                  | Weight loss, electrochemical techniques, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) studies. | Cathodic inhibitor, 250 ppm CeCl <sub>3</sub> and 250 ppm LaCl <sub>3</sub> shows highest IE and interpretation of inhibition mechanism.  | 14  |
| 15    | Carbon steel       | 60 ppm chloride media                   | Sodium dodecylsulphate (SDS)   | Zn <sup>2+</sup> | Weight loss study, FTIR and fluorescence spectra.   | Mixed-type inhibitor, IE 93%. Synergistic effect exists between SDS and Zn <sup>2+</sup> , and protective film consists of Fe <sup>2+</sup> -SDS complex.   | 15  |
| 16    | Al-Mg alloy AA5083 | 3.5% NaCl solution                      | CeCl <sub>3</sub>  |                  | Electrochemical noise measurements.   | The usefulness of robust statistical parameters, wavelet transform and transient shapes were illustrated.   | 16  |
| 17    | Zn                 | Aerated 0.5 M NaCl solution             | CeCl <sub>3</sub> and sodium octylthiopropionate (NaOTP)                                     |                  | Potentiostatic measurements, XPS and electron-probe microanalysis techniques.   | Synergistic effect exists between the inhibitors and combined IE is 95%.  | 17  |
| 18    | Fe                 | NaCl solution                           | Piperidin-1-yl-phosphonic acid (PPA) and (4-phosphono-piperazin-1-yl) phosphonic acid (PPPA) |                  | Potentiodynamic polarization study.   | Shifting of pitting potential in the positive direction and the decrease of corrosion current illustrates the inhibitive effect of the inhibitors and PPPA has better IE than PPA due to the adsorption of N(CH <sub>2</sub> ) <sub>2</sub> PO <sub>3</sub> H group on the metal surface. | 18  |
| 19    | Cu                 | NaCl solution                           | Imidazole derivative   |                  | Weight loss and electrochemical polarization studies.   | Inhibitors with a phenyl ring have better IE and obeys Freundlich adsorption isotherm.  | 19  |
| 20    | Brass              | Neutral aqueous NaCl solution           | N-[1-(benzotriazol-1-yl) methyl] aniline (BIMA) and 1-hydroxy methyl benzotriazole (HBTA)    |                  | Weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) and FTIR studies.                  | Mixed-type inhibitor, dezincification factor calculated and characterization of protective film.  | 20  |
| 21    | Al                 | Marine water (Cochin estuary)           | Cerium   |                  | Weight loss, linear sweep voltammetry, and potentiostatic polarization techniques.  | Cathodic inhibitor, protective layer consists of CeO <sub>2</sub> , Ce treatment on pure Al has significant corrosion inhibition.   | 21  |
| 22    | Cu                 | 0.1 M NaCl solution                     | Tannin (extracted from Tamarix articulata)   |                  | Polarization curves, impedance measurements and SEM studies.  | Anodic inhibitor, IE is 93.2% at concentration of 2g/l, protective film formation and explanation for the inhibition process.   | 22  |
| 23    | Carbon steel       | Neutral chloride solution               | N-phosphonomethyl-glycine (NPMG)   | Zn <sup>2+</sup> | Electrochemical impedance measurements, polarization curves, XPS and AES techniques.  | Mixed-type inhibitor, IE increases from 85 to 95% when inhibitor concentration increased from 10 to 100 mg/L and formation of protective film.  | 23  |
| 24    | Fe, Ni and Cu      | 3% NaCl solution                        | Calcium monofluorophosphate (CM)   |                  | Potentiodynamic polarization, open circuit potential, XPS and SEM techniques.   | Anodic inhibitor, Increasing concentration of inhibitor shifts corrosion potential in positive direction and formation of protective layer.   | 24  |
| 25    | Cu                 | 3% NaCl and 0.5 M HCl                   | Bis(1-benzotriazolyl-methylene)(2,5-thiadiazolyl)-disulfide (BBTD)                           |                  | Potentiodynamic polarization and FTIR techniques.   | Mixed-type inhibitor, BBTD behaves better in 3% NaCl than in 0.5 M HCl and protective layer consists of Cu(I).  | 25  |
| 26    | Cu-30Ni alloy      | 3% NaCl solution                        | 3-amino-1,2,4-triazole (ATA)   | Ammonia          | Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) and non-linear regression methods.              | Mixed-type inhibitor, IE is 98% which is enhanced in presence of ammoniac and kinetic parameters were evaluated from Levich-Koutecky relation.  | 26  |
| 27    | Fe                 | NaCl-bicarbonate solution and sea water | Phthalic acid and salicylic acid   |                  | Kinetic model experiment.   | Phthalate ion decreases the Fe(II) oxidation rate where as salicylate ion increases oxidation due to the formation of Fe(II)-salicylate complex.  | 27  |
| 28    | Cu                 | 3.0% NaCl solution                      | N-Phenyl-1, 4-phenylenediamine   | 1% EtOH          | Weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy, FTIR and UV-visible, SEM and EDAX studies. | Mixed-type inhibitor, protective film formation and the order of corrosion of Cu is oxygenated > aerated > deaerated solutions.   | 28  |

Table 1 (cont.). Corrosion inhibitors for seawater

| S.No. | Metal   | Medium                | Inhibitor  | Additive    | Method   | Findings   | Ref |
|-------|---|-----------------------|--|-------------|--|--|-----|
| 29    | Brass   | Artificial sea water  | N,N-dibenzotriazo[1,1- $\eta$ -methylaminomethane (DBMM) and 3-hydroxypropyl benzotriazole (HPBT)            |             | Weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), cyclic voltammetry and current transient techniques.                    | Mixed-type inhibitor, formation of protective film and inhibition of anodic dissolution of brass in artificial sea water effectively.  | 29  |
| 30    | Cu-Ni alloy   | 0.2 M NaCl solution   | Dodecylamine   |             | Potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and AFM studies.  | Cathodic inhibitor, IE increases with inhibitors concentration increased from 0.0005 M to 0.005 M and adsorption of dodecylamine on Cu-Ni alloy surface.   | 30  |
| 31    | Nickel plated copper  | 3.5% NaCl solution    | Polyaniline (PANI)   |             | Cyclic voltammetry, AC impedance spectroscopy (EIS) and polarization curves.   | PANI modified nickel plating provided much better barrier property to copper for longer periods.   | 31  |
| 32    | Carbon steel  | 3% NaCl solution      | TiO <sub>2</sub>   | dilute NaOH | Electrochemical impedance spectroscopy (EIS), coupling test, XRD and SEM techniques.   | Decrease of film resistance, film formed at 120 V can serve as photoanode and film accelerates the corrosion in the dark.  | 32  |
| 33    | Brass   | 0.10 M NaCl solution  | 2-[(E)-pyridin-2-ylimino]phenol (L <sub>1</sub> ) and 2-[(pyridin-2-yl-amino)methyl]phenol (L <sub>2</sub> ) |             | Potentiostatic polarization and AC impedance methods.  | IE increases with inhibitors concentration and protective film formation.  | 33  |
| 34    | Cu  | Sea water             | Poly(N-hexadecylamine)   | Docosanol   | Weight loss, potentiodynamic polarization and SEM studies.   | IE is 95%, stable and strong film formation over metal surface and obeys Langmuir-Blodgett adsorption isotherm.  | 34  |
| 35    | Mild steel  | Sea water             | Polyhydric alcohol phosphate ester (PAPE)  |             | Polarization curves, electrochemical impedance spectroscopy (EIS) and scanning tunneling microscopy (STM) studies.   | Mixed-type inhibitor, obeys Langmuir adsorption isotherm and complex film formation due to the interaction of R <sub>1</sub> function of PAPE and Fe <sup>2+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> , etc     | 35  |
| 36    | Cu  | 3.0% NaCl             | 2-amino-5-ethyl-1,3,4-thiadiazole (AETDA)  |             | Weight loss, pH, potentiodynamic polarization, potentiostatic current-time and electrochemical impedance spectroscopy (EIS), SEM and EDX studies.                | Mixed-type inhibitor, maximum IE is 97% at 5 x 10 <sup>-3</sup> M AETDA, protective film is formed due to strong adsorption of AETDA molecules and the order of IE is oxygenated > aerated > de-aerated solutions. | 36  |
| 37    | Al  | 0.50 M NaCl solution  | 1,4-naphthoquinone (NQ)  |             | Potentiodynamic polarization, chronoamperometry (CA), open-circuit potential (OCP), EIS, SEM, cyclic voltammetric, and quartz crystal analyzer (QCA) techniques. | NQ shows maximum inhibition at 1.0 x 10 <sup>-3</sup> M and protecting the pits on Al surface.   | 37  |
| 38    | Fe  | 0.1M NaCl solution    | Zinc chromate and zinc phosphate   |             | EIS, scanning vibrating electrode technique (SVET) and open circuit potential (OCP) measurements.  | Both inhibitors show lower inhibition efficiency.  | 38  |
| 39    | Cu  | Aerated NaCl solution | Sodium oleate (OA)   |             | Weight loss, potentiodynamic polarization and impedance measurements, SEM and EDX studies. Temperature: 15 – 65°C  | “Green” - Mixed-type inhibitor, formation of an adsorbed film on the metal surface, IE increases with inhibitor concentration and time of immersion and adsorption obeys Frumkin’s equation.                       | 39  |
| 40    | Galvanic electrode (N80 carb. steel (CS) + S31803 stainless steel (SS)) | 1% NaCl solution      | Dodecanoic acid and its sodium salt (DDAS)   |             | Electrochemical methods, FTIR and AFM studies. pH = 4.0  | Anodic inhibitor, protective layer formed on the metal surface due to the strong adsorption of the inhibitor and protective layer formed on the single CS electrode is less compact than that of on coupled CS.    | 40  |

Table 1 (cont.). Corrosion inhibitors for seawater

| S.No. | Metal  | Medium   | Inhibitor  | Additive            | Method   | Findings   | Ref |
|-------|--|--|--|---------------------|--|--|-----|
| 41    | Galvanic electrode (GE) (N80 carb. steel + S31803 stainless steel) | NaCl solution                                    | Imidazoline derivative (MAD)                             | KI                  | Electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, AFM and FTIR studies.                          | Cathodic inhibitors, synergistic effect exists between MAD and KI, and IE of MAD is higher in presence of KI due to the distribution of excess charge on the GE surface.   | 41  |
| 42    | N80 steel  | NaCl solution                                    | Quaternary alkoxymethyl amine (IMC-80-Q)                 | Ca <sup>2+</sup>    | Electrochemical impedance spectroscopy (EIS) and polarization resistance techniques. Temperature: 57°C                     | IMC-80-Q shows optimum inhibitor concentration significantly increased with the increase of Cl <sup>-</sup> concentration from 3% NaCl to 4.6% NaCl solution.  | 42  |
| 43    | Steel  | NaCl solution                                    | Cerium and lanthanum cinnamate                           |                     | Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy.   | The corrosion protection mechanism involves adsorption of the rare earth metal-cinnamate complex and oxide film on the steel surface.  | 43  |
| 44    | Mild steel   | 3% NaCl solution                                 | Polyaniline (PANI)                                       | Sodium benzoate     | Electrochemical impedance spectroscopy (EIS) and TGA.  | PANI/epoxy coating shows better IE than epoxy coating.   | 44  |
| 45    | Mild steel   | 3% NaCl solution                                 | Poly(N-methylamine) (PNMA) and poly(N-ethylamine) (PNEA) | Oxalic acid         | Electrochemical impedance spectroscopy (EIS) and DC polarization techniques.   | PNMA and PNEA exhibits effective anti-corrosive properties.  | 45  |
| 46    | Cu   | 3% NaCl solution                                 | 2-amino-5-(ethylthio)-1,3,4-thiadiazole (ATD)            |                     | Weight loss and pH measurements, potentiodynamic polarization, potentiostatic current-time, EIS, SEM and EDX studies.      | Mixed-type inhibitor, IE is 94% at 5.0 mM of ATD, strong adsorption of ATD molecules on copper surface and the order of IE is oxygenated > aerated > de-aerated media.   | 46  |
| 47    | Cu-Ni alloys   | Neutral chloride solution                        | Cysteine   |                     | Polarization and impedance techniques.   | 2.0 mM cysteine shows IE of 96%, strong physical adsorption of cysteine molecules on the alloy surface involves $\Delta G \sim -37.81$ kJ/mol.   | 47  |
| 48    | Cu, Zn, and Brass (Cu-10Zn and Cu-40Zn)                            | 0.5 M NaCl solution                              | Benzo-triazole (BTAH)                                    |                     | Electrochemical techniques, atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) studies.              | BTAH shows efficient inhibition, surface film (Cu <sub>2</sub> O, ZnO, Cu(I)-BTA and Zn(II)-BTA) provides effective barrier against corrosion.   | 48  |
| 49    | Cu   | 3.5% NaCl solution                               | 5-(Phenyl)-4H-1,2,4-triazole-3-thiol (PTAT)              |                     | Weight loss, potentiodynamic polarization, potentiostatic current time and pH measurements, and FTIR spectra.              | Mixed-type inhibitor, IE of 500 ppm PTAT is 13% only and that of 1500 ppm PTAT is 90%, pH values decreases with concentration of PTAT and protective film formed on copper surface due to the strong adsorption of PTAT molecules. | 49  |
| 50    | Cu   | Aerated synthetic sea water (3.5% NaCl solution) | 3-amino-1,2,4-triazole (ATA)                             |                     | Weight loss, electrochemical, gravimetric, pH measurements and Raman spectroscopy.   | IE increases with inhibitors concentration and a protective film is achieved by strong adsorption of ATA molecules on the metal surface.   | 50  |
| 51    | Cu-10Ni alloy  | 3.4% NaCl salt water                             | Benzo-triazole (BTAH)                                    | S <sup>2-</sup> ion | Optical and scanning electron microscopy (SEM) and X-ray diffraction (XRD) studies.  | BTAH has very high IE at the concentration above $5 \times 10^{-4}$ M and at lower concentration pitting corrosion occur.  | 51  |
| 52    | Cu   | 1.0 M NaCl solution                              | Purine (PU)  |                     | Weight loss, electrochemical polarization, electrochemical quartz crystal microbalance (EQCM) and SEM techniques. pH = 6.8 | IE increases with inhibitors concentration, adherent layer of inhibitor on metal surface account for the protective effect and chemical adsorption follows Langmuir isotherm.  | 52  |

Table 1 (cont.). Corrosion inhibitors for seawater

| S.No. | Metal                           | Medium                       | Inhibitor   | Additive                                       | Method  | Findings  | Ref |
|-------|---------------------------------|------------------------------|---|--|---|---|-----|
| 53    | Cu                              | 0.5 M NaCl solution          | 1-decanthiol (DT), 1,9-nonamedithiol (NDT) and 1,4-benzendimethanethiol (BDMT)  | Absolute EtOH, toluene, DMF, and acetonitrile. | Polarization, electrochemical impedance spectroscopy (EIS), cyclic voltammety, FTIR and AFM studies.                          | The order of IE is NDT > DT > BMDT and the solvent used for dissolving thiols have only a marginal effect on the IE.  | 53  |
| 54    | Steel                           | NaCl solution                | Polyvinyl alcohol   | Carbon black (CB)                              | Electrochemical impedance spectroscopy (EIS), polarization curves, immersion measurements and salt fog tests.                 | Composites coatings with CB nanoparticles reduced drastically the corrosion rate of steel.  | 54  |
| 55    | Carbon steel                    | Alkaline Cl-ion contg. water | Tungstate (WO <sub>4</sub> ) <sup>2-</sup> , molybdate (MoO <sub>4</sub> ) <sup>2-</sup> and nitrite (NO <sub>2</sub> ) <sup>-</sup> ions |  | Cyclic voltammety, potentiostatic current-time measurements, scanning electron microscopy (SEM), EDAX and XPS analysis.       | The rate of pit initiation decreases and the pitting potential moves to more positive direction upon the addition of inorganic anions and the order of pitting inhibition is (WO <sub>4</sub> ) <sup>2-</sup> > (MoO <sub>4</sub> ) <sup>2-</sup> > (NO <sub>2</sub> ) <sup>-</sup> . | 55  |
| 56    | Al alloy 2024-T3                | 3.5% NaCl solution           | 8-hydroxyquinoline (8HQ) and 8-hydroxy-quinoline-5-sulfonic acid (HQS)  |  | Open circuit potential, polarization measurements, electrochemical impedance spectroscopy (EIS) SEM and EDS studies.          | Mixed-type inhibitors, adsorption of 8HQ and HQS on metal surface forms a protective layer, 8HQ has better IE than HQS.   | 56  |
| 57    | Galvanized steel and mild steel | 0.5 M NaCl aqueous solution  | Polyurethane (PU)   |  | Electrochemical impedance spectroscopy (EIS)  | The relationship between the changes in mechanical properties and the degradation process were studied and PU coating shows higher adhesion and anticorrosion behavior.   | 57  |
| 58    | Carbon steel                    | Neutral solution             | Pimeloyl-1,5-di-hydroxamic acid (C7)  | Zn <sup>2+</sup> and Ni <sup>2+</sup>          | Surface analytical and electrochemical techniques.  | C7 offers effective corrosion inhibition in the presence of Zn <sup>2+</sup> and Ni <sup>2+</sup> due to the formation of stable slightly soluble complexes with these cations.   | 58  |
| 59    | Cu                              | 0.6 M NaCl and 1.0 M HCl     | Cysteine  |  | Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) studies.  | Maximum IE is 90%, decrease in corrosion current, shifting of corrosion potential in the negative direction and obeys Langmuir adsorption isotherm with $\Delta G \sim -25$ kJ/mol.   | 59  |
| 60    | Al alloy AA2014                 | 3.5% NaCl solution           | LaCl <sub>3</sub> and CeCl <sub>3</sub>   |  | Polarization and electrochemical impedance spectroscopy (EIS) and SEM studies.  | 1000 ppm of LaCl <sub>3</sub> and CeCl <sub>3</sub> shows significant corrosion inhibition, increase of double layer capacitance and film resistance, and film consists of precipitates of oxide/hydroxide of La and Ce.  | 60  |
| 61    | Mild steel                      | 0.01 M NaCl solution         | Lanthanum-4 hydroxy cinnamate   |  | Linear polarization resistance (LPR), cyclic potentiodynamic polarization (CPP) and EIS studies.                              | Anodic reaction strongly controlled and protective film formation.  | 61  |
| 62    | Carbon steel                    | Sea water                    | Hibiscus rosa-sinensis linn flower extract (FE)   |  | Weight loss, polarization and AC impedance, UV-visible and FTIR spectra and AFM studies.                                      | Mixed-type inhibitor and protective film consists of Fe <sup>2+</sup> -quercetin-3-O-glucoside complex.   | 62  |
| 63    | S37 Carbon steel                | Aerated NaCl solution        | Mixture of Cerium and Lanthanum oxides (2:1)  | AcOH   | Weight loss, potentiodynamic polarization, open circuit potential and constant potential measurements. Temperature: 25 – 70°C | The inhibitor is suitable for carbon steel in low to chloride media and 500 ppm of inhibitor concentration has maximum IE of 76%.   | 63  |
| 64    | Cu                              | 3% NaCl solution             | N-(5,6-diphenyl-4,5-dihydro-[1,2,4]triazin-3-yl)-guanidine (NTG)  |  | Weight loss, potentiodynamic polarization measurements, EIS and electrochemical frequency modulation (EFM) studies.           | IE is 99% and obeys Langmuir adsorption isotherm.   | 64  |
| 65    | Brass                           | 0.2 M NaCl                   | 2-mercaptobenzothiazole (MBT) and polyoxyethylene sorbitan monooleate (Tween-80).   |  | Potentiodynamic polarization, X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma analysis (ICP).           | Mixed-type inhibitor, MBT and Tween-80 shows IE's 79% and 62.5% and their combination shows IE 94% and synergistic effect controls dezincification of brass.  | 65  |

Table 1 (cont.). Corrosion inhibitors for seawater

| S.No. | Metal                     | Medium                   | Inhibitor  | Additive         | Method  | Findings  | Ref |
|-------|---------------------------|--------------------------|--|------------------|---|---|-----|
| 66    | 3003 Al alloy             | 0.5% NaCl solution       | Propargyl alcohol (PA) and Sodium potassium tartarate (SPT)                                      |                  | Electrochemical impedance spectroscopy (EIS) and Tafel polarization techniques.                                   | IE increases with inhibitors concentrations, PA and SPT shows significant synergistic effect and obeys Langmuir adsorption isotherm.  | 66  |
| 67    | Steel                     | Sea water                | Ca <sup>2+</sup> , Ni <sup>2+</sup> and Co <sup>2+</sup> naphthalates                            |                  | Electrochemical and stalagmometric methods.   | The natural naphthalates are very good inhibitors.  | 67  |
| 68    | Cu                        | 1.0 M NaCl solution      | Adenine (AD)   |                  | Weight loss, electrochemical polarization, electrochemical quartz crystal microbalance (EQCM) and SEM studies.    | IE increases with inhibitor concentration, adherent layer formed on the metal surface account for the protective effect, and chemical adsorption obeys Langmuir isotherm.   | 68  |
| 69    | Al alloy                  | Sea water                | Sodium benzoate  |                  | Potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and SEM studies.                       | Mixed-type inhibitor, the decrease of current density and double layer capacitance and increase of polarization resistance confirms the corrosion inhibition and protective film formation on the metal surface.  | 69  |
| 70    | Carbon steel              | Sea water                | Thiomorpholin-4-ylmethyl-phosphonic acid (TMPA) and morpholin-4-methyl-phosphonic acid (MPA)     |                  | Electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, FTIR, SEM and EDAX studies.           | Effective inhibitors, corrosion potential shifted in noble direction, IE is very high even at low concentration, and bonding mechanism between the metallic surface and the inhibitors.   | 70  |
| 71    | Armco Fe                  | 3% NaCl solution         | Piperidin-1-yl-phosphonic acid (PPA)   | Zn <sup>2+</sup> | Weight loss, potentiodynamic polarization and FTIR studies.   | IE of 0.005 M PPA is 76.7% where as that of 0.005 M PPA – 20% Zn <sup>2+</sup> is 90.2%, synergistic effect exists between PPA and Zn <sup>2+</sup> , and the protective film consists of Fe <sup>2+</sup> -PPA and Fe <sup>2+</sup> -PPA + Zn(OH) <sub>2</sub> in the absence and presence of Zn <sup>2+</sup> . | 71  |
| 72    | Mild steel                | 3% NaCl solution         | Sodium tripolyphosphate (STPP), sodium hexametaphosphate (SHMP) and adenosine triphosphate (ATP) | Zn <sup>2+</sup> | Weight loss, electrochemical polarization and SEM techniques. Temperature: 30, 40, and 50 °C                      | Mixed-type inhibitors, synergistic effect exists between phosphates and Zn <sup>2+</sup> , order of IE is STPP > SHMP > ATP, IE decreases with temperature, IE of STPP and SHMP increases with concentration and IE of ATP decreases with concentration.  | 72  |
| 73    | Cu, Fe and Cu-20%Fe alloy | 1.0 M NaCl solution      | Thiourea (TU)  |                  | Open-circuit potential measurements (OCP), polarization and electrochemical impedance spectroscopy (EIS) studies. | TU adsorbs at the alloy surface by Langmuir adsorption isotherm, IE is 91% and corrosion rate is in the order Cu < Cu-20%Fe < Fe.   | 73  |
| 74    | Carbon steel              | NaCl solution            | Yttrium (Y) and chromium (Cr)  |                  | Electrochemical measurements, Auger electron spectroscopy (AES) and XPS studies.                                  | Crevice corrosion resistance significantly improved, surface layer consists of Y <sub>2</sub> O <sub>3</sub> and Cr <sub>2</sub> O <sub>3</sub> and it acts as a barrier to reduce the corrosion.   | 74  |
| 75    | Carbon steel              | 5% NaCl aqueous solution | Polyaniline (PANI)   | EtOH             | Electrochemical corrosion measurements and Raman spectroscopy analysis.   | PANI-coated metal have excellent protection from corrosion and the passive layer over the surface consists of α-Fe <sub>2</sub> O <sub>3</sub> and Fe <sub>3</sub> O <sub>4</sub> .   | 75  |
| 76    | Steel                     | 3.5% NaCl solution       | Zinc aluminium polyphosphate (ZAPP) and zinc phosphate (ZP)                                      |                  | EIS, linear polarization (LP), SEM and EDX studies.   | The order of IE is ZAPP > ZP and formation of precipitated layer on the metal surface.  | 76  |
| 77    | Zn                        | Red sea water            | 2-mercaptotriazole   |                  | Cyclic voltammetry, SEM and EDAX studies.   | Mixed-type inhibitor and protective film formation.   | 77  |
| 78    | Brass-MM55 alloy          | Artificial sea water     | Benzotriazole  |                  | Dynamic electrochemical impedance spectroscopy (DEIS).  | Excellent inhibitor and DEIS is a relatively rapid measurement technique.   | 78  |
| 79    | 304 stainless steel       | 1.5% NaCl solution       | Ciprofloxacin and norfloxacin  |                  | Open circuit potential (OCP) and potentiodynamic polarization techniques.   | Both compounds act as anodic-type inhibitors and IE of norfloxacin is higher than ciprofloxacin.  | 79  |
| 80    | AISI/SAE Steel            | Sea water                | Sodium nitrite   |                  | Weight loss method  | Corrosion rate increases with time of exposure to the corrosive medium and 4% inhibitor in sea water shows optimum corrosion inhibition.  | 80  |

Table 1 (cont.). Corrosion inhibitors for seawater

| S.No. | Metal                      | Medium  | Inhibitor   | Additive | Method   | Findings  | Ref |
|-------|----------------------------|---|---|----------|--|---|-----|
| 81    | 90-10 Cu-Ni Alloy          | Sea water   | Thiosulphate  |          | Potentiodynamic polarization study. Temperature range: 25 and 50 – 80 °C   | At 25 °C, the corrosion rate increases with inhibitor concentration and at 50 or 80°C inhibitor forms a protective film that effectively decreases the corrosion rate.                                      | 81  |
| 82    | Brass-118                  | Artificial sea water                              | Benzotriazole (BTA)   |          | Dynamic electrochemical impedance spectroscopy (DEIS).   | Excellent inhibitor and DEIS is a very useful technique in the field of inhibitor research.   | 82  |
| 83    | AISI 430 stainless steel   | 3% NaCl solution                                  | Polyethylenesamines (PEI)   |          | Weight loss, polarization and cyclic polarization measurements and XPS technique.  | PEI provides the best protection against localized corrosion and acts as a diffusion barrier which follows physical adsorption.   | 83  |
| 84    | Cu                         | NaCl solution                                     | Benzotriazole, phenyl derivatives of tetrazole, bypyrazoles and 2-methyl-5-mercapto-1,3,4-thiadiazole.  |          | Scanning electron microscopy (SEM).  | The corrosion inhibition is due to the adsorption of inhibitor molecule on copper surface.  | 84  |
| 85    | ASTM 420 stainless steel   | 3% aqueous NaCl solution                          | Polyethyleneimine (PEI)   |          | Linear polarization, cyclic polarization, immersion tests and XPS studies.   | Very good inhibitor against pitting corrosion and a dense layer of PEI prevents the diffusion of ionic species from the film by chlorine from the salt water.   | 85  |
| 86    | Carbon steel               | 3% NaCl solution                                  | Poly (aniline-co-o-toluidine)   |          | Potentiodynamic polarization and EIS techniques and FTIR, UV-visible, TGA and XRD studies.   | Mixed-type inhibitor, IE is 70% at 100 ppm of inhibitor and obeys Temkin adsorption isotherm.   | 86  |
| 87    | Brass                      | 0.6 M NaCl solution                               | 2( $\beta$ -benzenesulphon-amido)ethylbenz-oxazole (I), 2( $\beta$ -benzenesulphonamido)-ethylbenzimidazole (II), 2( $\beta$ -benzenesulphonamido)ethylimidazole(III), 2( $\beta$ -benzenesulphonamido)ethyl-1,4,5,6-tetra-hydropyridimine (IV) |          | Gravimetric, Potentiodynamic polarization, AC impedance and EDS methods. pH: 6.0   | Very good mixed-type inhibitors, the order of IE is I<II<III<IV, the best IE is 77.6% and the inhibition is due to the formation of mixed ligand complex on the brass surface and blocking the active site. | 87  |
| 88    | Cu and brass               | Sea water   | Vitis vinifera (Extract prepared from seed and skin part of grapes)   | EtOH     | UV, FTIR and XRD studies. Temperature: 303 K, 313 K and 333 K respectively   | IE increases with inhibitor concentration but decreases with temperature and time, complex film formation, obeys Langmuir and Temkin adsorption isotherms.  | 88  |
| 89    | Cu and its alloy (Cu-27Zn) | Sea water   | Embliea officinalis leaves extract  |          | UV and IR studies. Temperature: 303 and 333 K, respectively  | Physical adsorption obeys Langmuir and Temkin isotherms, which are exothermic and spontaneous.  | 89  |
| 90    | Brass alloy                | Mediterranean sea water (MSW) and oil field water | Benzotriazole (BTAH)  |          | Weight loss, potentiodynamic polarization, X-ray diffraction (XRD) and SEM studies.  | Mixed-type inhibitor, formation water is more corrosive for brass alloy than sea water, excellent control of dezincification of brass and IE ~ 98.15% for formation water at optimum concentration.         | 90  |
| 91    | Cu                         | 3.5% NaCl solution                                | 2-mercapto-4-(p-methoxyphenyl)-6-oxo-1,6-dihydropyridimine-5-carbonitrile (MPD)   |          | Electrochemical frequency modulation (EFM), electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and molecular stimulation (MS) techniques   | Mixed-type inhibitor, IE increases with inhibitor concentration and the number of electrons transferred from MPD to metal surface calculated by semi-empirical quantum chemical calculations.               | 91  |
| 92    | Cu                         | 3.5% NaCl solution                                | 1-phenyl-2,4-dithiobiuret (Inh I), 1-p-methoxyphenyl-2,4-dithiobiuret (Inh II) and 1-p-chlorophenyl-2,4-dithiobiuret (Inh III).   |          | Weight loss, electrochemical impedance spectroscopy, polarization curves, SEM and ESCA studies.  | The order of IE is Inh II > Inh I > Inh III and the inhibition is due to the formation of protective film consist of Cu(I)-inhibitor complex, CuCl or CuCl <sub>2</sub> complex ions.                       | 92  |
| 93    | Cu                         | Aerated 0.1 M NaCl solution                       | 8-aminoquinoline (8-AQ)   |          | Open circuit potential (OCP), potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements, and atomic force microscopy (AFM) study. | Mixed-type inhibitor at concentration higher than 10 <sup>-3</sup> M, a film formed of thickness 10 µm and the interaction between 8-AQ and copper surface is most probable.                                | 93  |



Table 1 (cont.). Corrosion inhibitors for seawater

| S.No. | Metal            | Medium  | Inhibitor  | Additive        | Method  | Findings   | Ref |
|-------|------------------|---|--|-----------------|---|--|-----|
| 94    | Cu               | 3.5% NaCl solution  | 2,5-dimercapto-1,3,4-thiadiazole   |                 | Weight loss, potentiostatic polarization, AC-impedance, UV-visible, FTIR, ESCA and SEM studies.<br>pH = 6.5, 7.0 and 9.0                  | Mixed-type inhibitor, IE at pH 7.0 is 94.5% and formation of protective film consist of Cu(II)-inhibitor complex, CuCl or CuCl <sub>2</sub> complex ions or both and no oxide on metal surface.  | 94  |
| 95    | Al-Si alloy      | 3.5% NaCl solution  | Alumina  |                 | Potentiostatic polarization, EIS, SEM and XRD studies.<br>Temperature: 25°C and 300°C<br>pH = 4.0   | Non-porous protective coating of thickness around 7µm, higher corrosion resistance and a significant decrease in diffusion of chloride ion through metal.  | 95  |
| 96    | Carbon steel     | 200 mg L <sup>-1</sup> NaCl solution  | Activated starch (AS) and carboxymethylated starch (CMS)   |                 | <sup>13</sup> C NMR, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and AFM studies.                          | Modified starches have corrosion inhibitive properties, AS shows better IE than CMS, IE depends on degree of substitution, strong ionic interaction between AS and Fe <sup>2+</sup> ions, and higher protection is due to the densification of the inhibitive layer. | 96  |
| 97    | Brass            | 0.6 M NaCl solution   | Glycine (I), L (-)-aspartic acid (II), glutamic acid (III), N-benzenesulphonyl glycine (IV), N-ben-zenesulphonyl-L (-)-aspartic acid (V) and N-benzenesulphonyl-L (-)-glutamic acid (VI) |                 | Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques.<br>pH = 6.0                                     | Mixed-type inhibitors, order of IE is I<II<III<IV<V<VI, IE is maximum at 4 x 10 <sup>-5</sup> M concentration, IE increases due to the π electron contribution of the benzene ring and presence of more adsorption sites,  | 97  |
| 98    | Fe               | 30 mg L <sup>-1</sup> NaCl + 70 mgL <sup>-1</sup> Na <sub>2</sub> SO <sub>4</sub> | Sodium benzoate (SB)   |                 | Tafel polarization curves, electrochemical impedance spectroscopy (EIS), XRD and SEM studies.   | IE of SB increases as the grain size decreased from microcrystalline to nanocrystalline and it is associated with the increase of the surface energy.  | 98  |
| 99    | Steel            | Salt water saturated with CO <sub>2</sub>   | Hydroxyethyl imidazole   |                 | Polarization curves, linear polarization curves, EIS and electrochemical noise studies.<br>Temperature: 50°C                              | Anodic inhibitor, best IE at 25 ppm and protective film formation.   | 99  |
| 100   | Mild steel       | 8.6 mM NaCl solution  | Molybdate (MoO <sub>4</sub> ) <sub>2-</sub> and nitrite (NO <sub>2</sub> ) <sup>-</sup> ions   |                 | X-ray photoelectron spectroscopy (XPS) technique.<br>pH = 8.0   | Anion films are ~ 5 nm deep, film consists of ferric molybdate and nitrite respectively.   | 100 |
| 101   | 3003 Al alloys   | Sea water   | Calcium nitrite  |                 | Cyclic polarization testing and SEM studies.  | Formation of protective oxide layer and increase in the amount of inhibitor leads to pitting corrosion.  | 101 |
| 102   | Cu               | 3% NaCl solution  | N-decyl-3-amino-1,2,4-triazole   |                 | Potentiodynamic measurements, electrochemical impedance spectroscopy (EIS), SEM and EDAX studies.   | Mixed-type inhibitor and IE increases with inhibitor concentration.  | 102 |
| 103   | Al               | Arabian Gulf Sea water (AGS) and 3.5% NaCl solution.                              | 3-amino-5-mercapto-1,2,4-triazole (AMTA)   |                 | Cyclic potentiodynamic polarization (CPP), Chronoamperometric current-time and electrochemical impedance spectroscopy (EIS) measurements. | AGS is more corrosive than 3.5% NaCl solution and IE of AMTA is higher for AGS than 3.5% NaCl solution.  | 103 |
| 104   | Brass            | Sea water (Eliot beach-southern coast of Chennai, India)                          | 2-amino-5-ethyl-1,3,4-thiadiazole (AETD), 2-amino-5-ethylthio-1,3,4-thiadiazole (AETTD) and 2-amino-5-tert-butyl-1,3,4-thiadiazole (ATBTD)   |                 | Potentiodynamic polarization, EIS, inductively coupled plasma atomic emission spectroscopy (ICP-AES) and SEM, EDAX and FTIR studies.      | Mixed-type inhibitors, IE% increases with inhibitor concentration, obeys Langmuir adsorption isotherm, control of cathodic reaction and dezincification of brass.  | 104 |
| 105   | Cu/70-30Ni alloy | Aerated 3% NaCl solution  | 3-amino-1,2,4-triazole (ATA), 3-4'-bitriazole-1,2,4 (BITA) and 2-mercaptobenzimidazole (MBI)   | NH <sub>3</sub> | Potentiodynamic measurements, electrochemical impedance spectroscopy (EIS) and SEM studies.   | Mixed-type inhibitor controls both anodic and cathodic reactions and IE increases with inhibitors concentrations and corrosion rate decreases.   | 105 |

Table 1 (cont.). Corrosion inhibitors for seawater

| S.No. | Metal            | Medium                     | Inhibitor   | Additive         | Method   | Findings  | Ref |
|-------|------------------|----------------------------|---|------------------|--|---|-----|
| 106   | Mild steel       | 3.5% NaCl solution         | Zinc acetate (ZA), zinc acetylacetonate (ZAA) and zinc gluconate (ZG)   |                  | Electrochemical impedance spectroscopy (EIS), pH, XRD and SEM techniques.  | ZG shows better IE than the others and it forms insoluble protective film over metal surface  | 106 |
| 107   | Al-Cu alloy      | Chloride solution          | Cerium diphenyl phosphate (Ce(dpp) <sub>2</sub> )   |                  | SEM and ToF-SIMS coupled with electrochemical impedance spectroscopy (EIS) measurements.                                 | Strong corrosion inhibitor and formation of a protective complex oxide film of Al and Ce.   | 107 |
| 108   | Cu               | 3% NaCl solution           | N,N-bis (3-carbomethoxy-5-methylpyrazol-1-ylmethyl) cyclohexylamine (BiPyA)   |                  | Potentiodynamic polarization and linear polarization (LRP) techniques.   | Efficient mixed-type inhibitor, IE's from Tafel plots and LRP method are in good agreement and BiPyA adsorbed on the copper surface according to Langmuir isotherm.   | 108 |
| 109   | Brass            | 0.6 M NaCl solution        | $\alpha$ -benzenesulphon-amido- $\beta$ -(2-imidazolyl)ethanoic acid (R <sub>1</sub> H) and 1-benzenesulphonamido-1,2-bis(2-imidazolyl)-ethane (R <sub>2</sub> H) | Cysteine         | Potentiodynamic polarization and electrochemical AC impedance studies.<br>pH = 6.0                                       | Very good mixed-type inhibitors and antifouling agents, IE of the two inhibitors is higher than 80%, order of IE is R <sub>2</sub> H > R <sub>1</sub> H and IE of R <sub>1</sub> H is increased due to synergistic effect of cysteine and this effect was not observed in case of R <sub>2</sub> H. | 109 |
| 110   | Galvanneal steel | 0.1 M NaCl solution        | Cerium (IV) oxide   | SiO <sub>2</sub> | Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).   | Cathodic inhibitor and mechanical treatment performed on the CeO <sub>2</sub> and SiO <sub>2</sub> particles promote the formation of an effective corrosion pigment.   | 110 |
| 111   | Al alloy 2024-T3 | 0.05 M NaCl solution       | Cerium cinnamate (CC)   |                  | Polarization measurements, immersion tests, XPS and electron-probe microanalysis (EPM).                                  | Anodic inhibition is due to the deposition film and protection mechanism involves deposition of CC and then hydrolysis of cerium ions to form Cerium oxide/hydroxide.   | 111 |
| 112   | Carbon steel     | Alkaline chloride solution | 1-butyl-3-methyl-imidazolium tetrafluoroborate ([BMIM][BF <sub>4</sub> ])   |                  | Electrochemical measurements, AFM and XPS studies.   | Mixed-type inhibitor, obeys Langmuir adsorption isotherm, inhibitor controls anodic and cathodic processes effectively and blocks the access of chloride ions to the metal surface.   | 112 |
| 113   | Carbon steel     | NaCl solution              | Mussel adhesive protein (Mefp-1) (derived from marine mussel <i>Mytilus edulis</i> )  |                  | Electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and AFM studies.<br>pH = 4.6                  | Mefp-1 confers significant corrosion inhibition, within a short exposure time, the IE is increases with chloride concentration, but for longer exposure the IE is increases with lower chloride concentration and the protective film consists of bovine serum albumin (BSA).                       | 113 |
| 114   | Cu               | 3.5% NaCl solution         | 2-carboxymethylthio-4-(p-methoxyphenyl)-6-oxo-1,6-dihydro-pyrimidine-5-carbo-nitrile (CPD)  |                  | Electrochemical frequency modulation (EFM), EIS, potentiodynamic polarization and molecular stimulation (MS) techniques. | Mixed-type inhibitor, IE increases with inhibitor concentration and adsorption obeys Langmuir isotherm.   | 114 |
| 115   | Carbon steel     | 0.5 M NaCl solution        | Thiadiazole derivatives   |                  | Open circuit potential (OCP), Tafel polarization, electrochemical impedance spectroscopy (EIS) and SEM techniques.       | Anodic inhibitor, IE increases with inhibitor concentration and decreases with temperature, obeys follows Langmuir isotherm and inhibitor acts as retarding catalyst for pitting corrosion.   | 115 |
| 116   | Cu               | 3.5% NaCl solution         | Fungicides (myclobutanil and hexaconazole)  |                  | Weight loss, electrochemical measurements, SEM and EDX studies.  | Mixed-type inhibitors, obeys Langmuir adsorption isotherm and good performance at different temperatures.   | 116 |

## pH

The IE of various inhibitors have been evaluated at neutral pH,<sup>1-39, 41, 53-86, 88-93, 96, 98, 99, 101-108, 110-112, 114-116</sup> and also at pH 4.0,<sup>40, 95</sup> 6.8,<sup>52</sup> 6.0,<sup>87, 97, 109</sup> 6.5, 7.0 and 9.0,<sup>94</sup> 8.0<sup>100</sup> and 4.6<sup>113</sup>.

## Methods

Various methods have been used to evaluate the IE of inhibitors. Usually, weight loss method,<sup>1, 2, 5, 6, 8, 10, 13-15, 19-21, 28, 29, 34, 39, 46, 49, 50, 52, 54, 62-64, 68, 71, 72, 80, 83, 85, 90, 92, 94, 111, 116</sup> pH variation,<sup>36, 46, 49, 106</sup> potentiodynamic polarization,<sup>3-10, 12, 14, 17-26, 28-31, 33-37, 39-42, 45-50, 52-56, 58-76, 79, 81, 83, 85-87, 91-99, 101-105, 108-116</sup> electrochemical impedance spectroscopy,<sup>6, 7, 10-12, 14, 20, 22, 23, 26, 28-33, 35-38, 40-42, 44-48, 50, 52, 54, 56-62, 64, 66, 67, 69, 70, 73, 74-76, 78, 82, 86, 87, 91-99, 102-107, 109, 110, 112-116</sup> open circuit potential,<sup>24, 37, 38, 56, 63, 73, 79, 93, 115</sup> chronoamperometry,<sup>37, 103</sup> inductively coupled plasma atomic emission spectroscopy,<sup>65, 104</sup> cyclic voltammetry,<sup>7, 9, 21, 29, 31, 37, 53, 55, 77</sup> electrochemical frequency modulation,<sup>64, 91, 114</sup> quartz crystal analysis,<sup>37, 52, 68</sup> molecular stimulation,<sup>91, 114</sup> gravimetry,<sup>87</sup> thermogravimetric analysis,<sup>44, 86</sup> stalagmometry,<sup>67</sup> electrochemical noise analysis,<sup>11, 16, 99</sup> electron probe microanalysis,<sup>17, 111</sup> coupling test,<sup>32</sup> kinetic model technique,<sup>27</sup> capillary gas chromatography,<sup>1</sup> growth curve method,<sup>1</sup> and scanning vibrating electrode technique<sup>38</sup> have been employed.

## Adsorption isotherms

The adsorption behaviour of the atoms/ingredients present in the inhibitor over the metal surface has been investigated and the type of adsorption isotherm such as Langmuir adsorption isotherm,<sup>2, 5, 10, 12, 34, 35, 52, 59, 64, 66, 68, 73, 88, 89, 104</sup> Freundlich adsorption isotherm,<sup>19</sup> Frumkin adsorption isotherm,<sup>39</sup> and Temkin adsorption isotherm,<sup>86, 89</sup> have been proposed, and it is supported by various thermodynamic parameters such as changes in free energy, enthalpy and entropy.

## Surface analysis

The protective films formed on metal surface, during the process of corrosion protection of metals by inhibitors, have been analyzed by various surface morphological studies such as UV-visible spectroscopy,<sup>10, 28, 62, 86, 88, 89, 94</sup> fluorescence spectroscopy,<sup>4, 13, 15</sup> Raman spectroscopy,<sup>50, 75</sup> FTIR,<sup>7, 13, 15, 20, 25, 28, 41, 43, 49, 53, 62, 70, 71, 86, 88, 89, 94, 104</sup> EDX,<sup>14, 28, 39, 46, 55, 56, 70, 76, 77, 87, 102, 104, 116</sup> XRD,<sup>2, 10, 13, 32, 51, 86, 88, 90, 95, 98, 106</sup> Auger electron spectroscopy,<sup>6, 23, 74</sup> XPS,<sup>12, 17, 23, 24, 48, 55, 65, 74, 83, 85, 100, 112</sup> ESCA,<sup>92, 94</sup> STM,<sup>12, 35</sup> SEM,<sup>10, 14, 22, 24, 28, 32, 34, 39, 46, 51, 52, 55, 56, 60, 68-70, 72, 76, 77, 84, 90, 92, 94, 95, 98, 101, 102, 104-107, 115</sup> and AFM.<sup>30, 41, 48, 53, 62, 93, 96, 112, 113</sup> It has been observed that the protective film consists of the metal-inhibitor complex at the anodic sites of metal surface and in some cases, Zn(OH)<sub>2</sub> is deposited on the cathodic sites of the metal surface, if Zn<sup>2+</sup> is used along with the inhibitor.

## Plant and animal materials

Extracts of various parts of the plants such as leaves,<sup>89</sup> flowers<sup>62</sup> and seeds,<sup>22, 88</sup> and animal products such as honey,<sup>5</sup> protein<sup>113</sup> and fungicides<sup>116</sup> have been used as

corrosion inhibitors since they are eco-friendly, non-toxic, bio-degradable and cost effective.

## Solvents

Solvents such as water<sup>5, 22, 62, 89</sup> and ethanol,<sup>88</sup> have been used to extract the ingredients present in plant and animal products.

A list of various inhibitors that have been used as corrosion inhibitors for sea water is given in Table 1.

## Conclusion

This review paper will be useful to a researcher who would like to select inhibitors to control corrosion of metals and its alloys in sea water. Especially this will be useful, when sea water is used in cooling water system.

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