CHAPTER-II

REVIEW OF LITERATURE

Several inhibitors have been used for cooling water systems. Many chemical compounds singly or in formulations can be used as corrosion inhibitors, particularly for steel in near neutral, aqueous solutions. Such compounds include chromates, nitrites, phosphates phosphonates and carboxylates of various molecular structures.

The principles and practice of corrosion inhibition in recent years have become conscious to health and safety considerations. These relate to all aspects of inhibitor practice i.e., handling, storage, use and disposal. The use of hazardous chemicals has been restricted to limited use with no contact with environment. The use of chromates and phosphates is restricted due to the environmental health hazard. Hence there is a need for the use of non-toxic, ecofriendly corrosion inhibitors. Carboxylic acids, their salts and their derivatives have recently emerged as a new and potential class of corrosion inhibitors. Many carboxylates such as salicylate\(^1\), cinnamate\(^2\), phenyl acetate\(^3\), anthranilates\(^4\), thio divalerate\(^5\), adipate\(^6,7\) and their derivatives have been used as inhibitors. Their inhibitive action results from the bonding of the anion to the metal surface through the excess e’s on the O \(^-\). Inhibitive anions such as benzoate, phthalate and other carboxylates stabilize the oxide film on iron surface\(^8,9,10\). Review of carboxylates as corrosion inhibitors have appeared from time to time\(^11-14\). Mercer\(^15\) reviewed carboxylates that provide protection to cast iron and non–ferrous metals in 1980.

Review of literature reveals the use of many organic acids, their salts or their derivatives as corrosion inhibitors to various metals and alloys like Cu, Al carbon steel, stainless steel etc., in various aqueous media (acids, alkaline and neutral).
II.1: Amino acids and their derivatives as corrosion inhibitors:

Bereket and Yurt\textsuperscript{16} have studied the inhibition effect of amino acids and hydroxy carboxylic acids on pitting corrosion of Al alloy in NaCl solution at various pH levels by potentiostatic methods. Amino acids shift the $E_{\text{pit}}$ values to noble direction in acidic solutions, while hydroxy carboxylic acids are effective in neutral and basic solutions.

Yurt and Bereket\textsuperscript{17} have correlated the experimentally obtained inhibition efficiencies of six amino acids and six hydroxy carboxylic acids for the corrosion of Al alloy 7075 in NaCl with parameters such as electronic charge on active centers, dipole moment, highest occupied and lowest unoccupied molecular orbital energies etc based on quantum chemical calculations. Aksut and Bilgic\textsuperscript{18} have examined the inhibitive effect of amino acids on the passivity of Ni in H$_2$SO$_4$.

According to Pech and Bartolo\textsuperscript{19} the inhibitive effect of N-phosphonomethyl glycine-Zn$^{2+}$ mixture on corrosion of steel in neutral medium is due to the retardation of anodic and cathodic processes due to the film, Fe-inhibitor complex and ZnO. Zerfaoui et al\textsuperscript{20} have reported the corrosion behavior of pure iron in citric acid in the presence of glycine, leucine, aspartic acid, arginine, and methionine and they were found to act as cathodic inhibitors. Abd-El-Nabey et al\textsuperscript{21} have investigated the influence of amino acids such as cysteine, cystine, and methionine as corrosion inhibitors on the corrosion of carbon steel in acid medium. Both anodic and cathodic polarization curves were found to be affected. Amino carboxylic acids and their N-phosphonomethyl derivatives with or without additives (Zn or metavanadate ion) have been studied in neutral solution by Kalman et al\textsuperscript{22} Ashassi et al have investigated the inhibitive action of alanine, glycine and leucine by potentiodynamic and polarization methods towards the corrosion of steel\textsuperscript{23} and Al\textsuperscript{24} in acid medium. Gamal and Mostaf\textsuperscript{125} have elucidated the effect of temperature and the molecular
structure of amino acids on the inhibition efficiency for the corrosion inhibition of Cu electrode in 1M HCl solution.

II.2. Poly carboxylic acids and their derivatives as corrosion inhibitors:

Polymer having COOH group is one of the effective polymer based system. There are several carboxylic acids of low molecular weight, which are used as corrosion inhibitor to many inhibitor formulations. Rajendran et al\textsuperscript{26} Aramaki\textsuperscript{27} and Yuasa et al\textsuperscript{28} have studied the inhibitive effect of polyacrylate, polymaleic and polymethacrylate along with other inhibitors. According to Yuasa et al\textsuperscript{29} the inhibitive effect of polyacrylic acid–polyacrylamide is due to the formation of polymer-polymer complex.

Bodo Muller et al\textsuperscript{30} have studied the corrosion inhibition of polymethacrylic acid and styrene maleic acid co-polymer on zinc pigments in aqueous alkaline medium. Abd El Rehim et al\textsuperscript{31} have discussed that the amino polycarboxylic acids such as Ethylene glycol-bis (1-aminoethylether-N, N)tetraacetic acid, diethylene triaminepentaacetic acid, ethylene diaminetetraacetic acid and nitrilo acetic acid inhibit corrosion of steel in sulphate solutions at low pH and promote corrosion above certain pH. An alkaline cooling water treatment program with ATMP and sodium polyacrylate has been reported.\textsuperscript{32} The performance of HEDP and acrylic acid base terpolymer have been evaluated.\textsuperscript{33}

Bodo Muller\textsuperscript{34} has studied the corrosion inhibition of Al by various polymers such as polyacrylic acid, styrene-maleic acid, styrene-acrylate co-polymer, phenolic resins and polyvinyl alcohol (PVA). According to him ionic interactions between the metal and inhibitor are essential for corrosion inhibition. The behaviour of corrosion inhibition by various cationic polymers such as polyethyleneimine derivative, polyacrylamide derivative, polydicyandiamide derivative and anionic polymers such as polymaleic acid derivative, polyacrylic acid derivative and polyacrylic acid was investigated by
Sekine et al\textsuperscript{35}. Shah et al\textsuperscript{36} have discussed the use of antifoulants such as sodium acrylate, sodium salt of polymaleic acid, carboxymethyl cellulose (CMC) and tannin for clay and CaCO\textsubscript{3} dispersion.

\textbf{II.3. Substituted acids and their derivatives as corrosion inhibitors:}

Nathalie Ochoa\textsuperscript{37} et al have studied the influence of fatty amines in association with phosphono carboxylic acid salts on the corrosion of carbon steel. Electrochemical studies\textsuperscript{38} of the corrosion inhibition of methionine ethyl ester of iron in citric chloride solution has revealed that it is a mixed type indicator and it acts on the cathodic reactions without changing the mechanism of hydrogen evolution. Hydrazides of carboxylic acids\textsuperscript{39} were found to act as inhibitors, for the corrosion of steel in acidic medium.

Ethoxylated fatty acids were found to act as corrosion inhibitor for carbon steel in formation water\textsuperscript{40}, for zinc in acidic medium\textsuperscript{41}, Al in acidic medium\textsuperscript{42} and mild steel in acidic medium.\textsuperscript{43} Three long chain fatty acids\textsuperscript{44} namely 2-undecane-5-mercapto-1-oxa-3,4-diazole (UMOD), 2-heptadecene-5-mercapto-1-oxa-3,4-diazole (HMOD) and 2-decene-5-mercapto-1-oxa-3,4-diazole (DMOD) were found to act as mixed type of inhibitors for mild steel in acidic medium. Adsorption mechanism was proposed.

Electrochemical studies were carried out on the influence of [(2-pyridine-4-ylethyl) thio] acetic acid and pyridine on the corrosion of steel in H\textsubscript{2}SO\textsubscript{4} solution by Boukla\textsuperscript{45}. The influence of diethyl pyrazine-2,3-dicarboxylate on the corrosion of steel in 0.5 M H\textsubscript{2}SO\textsubscript{4} solution was studied by Boukla\textsuperscript{46} using mass-loss and electrochemical methods. It is reported that the inhibitors act essentially as a cathodic inhibitor.

Agarwal and Landolt\textsuperscript{47} have concluded that the inhibition efficiency of N-ethyl-morpholine salts of a \& omega; - benzoyl alcanoic acid and benzoic acid is the result of the passivation of the electrode due to the capacity of these
inhibitors to act as a buffer in the anodic diffusion layer, thus blocking the surface sites for anodic dissolution. Radusev et al have studied the inhibitive effect of hydrazides of fatty carboxylic acids on the corrosion of steel in HCl, H$_2$S and actual oil field water.

A comparative study of the inhibitive effect of omega; benzoyl alcanoic acid with benzoic acid for the corrosion of steel in different electrolyte was carried out by Agarwal and Landolt.\textsuperscript{49} The inhibition of corrosion of mild steel in H$_2$SO$_4$ by commercial surfactants alkyl phenyl ethoxide-2000 and alkyl phenyl ethoxylate-400 has been studied\textsuperscript{50} and they are found to be mixed inhibitors. Seliman et al\textsuperscript{51} have studied the inhibitive action of sodium ethoxylates of soya bean oil towards the corrosion of zinc in 2M H$_2$SO$_4$ using thermometric methods. The results show that the retardation of metal dissolution is due to chemisorption.

Karthikeyan et al\textsuperscript{52} have studied the influence of anions such as chlorides and sulphates in the performance of thiomalic acid as an inhibitor for the corrosion of mild steel in HCl and H$_2$SO$_4$ and in their studies they have reported that thiomalic acid brings down the hydrogen permeation through mild steel in both acids. Milan Bartus et al\textsuperscript{53} have investigated the corrosion inhibition of mild steel in CO$_2$ saturated synthetic brine by low molecular weight organic acids containing sulphur in their molecular structure such as thioglycollic acid. Phosphonates terminated carboxylate –based telomers have been used as scale/corrosion inhibitors and /or fouling agents in aqueous system\textsuperscript{54}. Corrosion inhibition of carbon steel by 2-phosphonobutane-1,2,4-tricarboxylic acid is based on the formation of an inhibiting film.\textsuperscript{55}

It has been reported that corrosion of carbon steel can be inhibited by the addition of organic phosphono carboxylic acid (e.g., 2-phosphonobutane-1, 2,4-tricarboxylic acid and/or phosphino carboxylic acid and manganese\textsuperscript{56}. Corrosion inhibiting compositions containing carboxylated phosphonic acid (hydroxy
phosphonoacetic acid or 2- phosphonobutane- 1, 2,4-tricarboxylic acid) and a sequesterant selected from tartaric acid, citric acid, and gluconic acid have been studied\textsuperscript{57}.

A corrosion inhibitor for iron based alloys in an aqueous system (tap water) comprises of hydroxy phosphonoacetic acid or its water soluble ammonium or alkali metal salt and co-polymer formed from 2-acrylamido-2-methylpropane sulphonic acid and acrylic acid or methacrylic acid has been developed.\textsuperscript{58} Aramaki\textsuperscript{59, 60} has reported that the film of 1, 2-bis(triethoxysilyl)ether polymer containing sodium octylthiopropionate (NaOTP) prevented corrosion of iron at scratched surface in aerated NaCl solutions. X-ray, photo electron spectroscopy and electron probe micro analysis of the surface have revealed that the corrosion at scratch was suppressed by the formation of iron oxide layer containing a small amount of complex formed by NaOTP with Fe\textsuperscript{3+}.

Malik\textsuperscript{61} has investigated the effect of pH on the performance of tertiary amines possessing a single carboxylic acid group for the corrosion of mild steel in CO\textsubscript{2} saturated brine solution. It is reported that at pH 6.5, the inhibition is primarily due to the attachment of O\textsuperscript{-} at anodic site while at pH 3.9, corrosion rate decreases as a result of the inhibitor loosely lying flat at the metal solution interface. Malik\textsuperscript{62} has reported that negatively charged species exhibit better inhibition efficiencies at pH 6.5 while positively charged species show better inhibition efficiencies at pH 3.9.

According to Kunitsugu Aramaki\textsuperscript{63} the inhibition effect of organic inhibitors such as sodium benzoate, sodium N-dodecanoyl sarcosinate, sodium S-octyl-3-thiopropionate and 1,2,3-benzotriazole are due to the formation of film containing zinc salts or complexes together with Zn(OH)\textsubscript{2}. The film was analysed by X-ray, photoelectron and Fourier transform infrared reflection spectroscopy. Sakthivel et al\textsuperscript{64} have evaluated the corrosion inhibition properties of ethyl-1,2-N-diphsophonomethylamino diethanoic acid for mild steel in cooling water.
Based on gravimetric, cathodic Tafel plots, linear polarization resistance and EIS methods, Chetouani et al have concluded that the inhibiting effects of N,N-bis[(3,5-dimethyl-1H-pyrazol-1-yl)methyl]-N-(4-methylphenyl)amine (P₁) and methyl-1-[((methylphenyl){[3-(methoxycarbonyl)-5-methyl-1H-pyrazole-1-yl] methyl} amino)methyl]-5-methyl-1H-pyrazole-3-carboxylate (P₂) on corrosion of pure iron in 1M HCl are due to adsorption of the inhibitor on the metal surface which obeys Langmuir adsorption isotherm and they act as mixed inhibitors.

Nathalie et al have reported that the inhibition efficiency of the inhibitor system consisting of fatty amines and phosphonocarboxylic acid salts are due to the formation of the chelates between the phosphonocarboxylic acid salts and Fe oxide / hydroxide.

**II.4. Simple Aromatic carboxylic acids and their derivatives as corrosion inhibitors:**

Bilgic has reported that benzoic acid acts as a better inhibitor for the corrosion of steel in sulphuric acid, compared to salicylic acid with the same concentration. Both the inhibitors obey Langmuir isotherm. Maria Forsyth et al have established the existence of synergism between Ce⁢³⁺ ion and salicylate anion, in their study on corrosion inhibition of mild steel surfaces by cerium salicylate. Blustein et al have proposed adsorption mechanism for the inhibitive properties of calcium benzoate for steel corrosion in NaNO₃ solutions. Faidi and Scantlebury have studied the corrosion behaviour of mild steel in single-phase glycol–ether-water mixture on the addition of NaNO₂, sodium benzoate and benzylamine.

Turgoose in his article on the influence of sodium benzoate on corrosion of steel has concluded that too low or too high content of benzoate leads to corrosion. The influence of aggressive ions on the corrosion of iron in the presence of benzoate anion has been reported.
The effects of polyhydroxy carboxylates, and benzoate on pitting corrosion of steel were studied using cyclic anodic polarization measurements in chloride solutions. Fouda et al. have studied the effects of phthalimide derivatives on the corrosion behaviour of Cu in nitric acid.

The inhibitive action of benzoic acid and its derivatives on dissolution of Al and Cu in HNO₃ is studied by Agrawal et al. Moussa et al. have explained that the inhibition efficiency of aromatic acids depends on the number and position of the carboxylic group and other substituents in the benzene ring; Inhibition efficiency is higher in NaOH than HCl. For aliphatic carboxylic acids, the increase in chain length increases the inhibitive power. Fokin et al. have related the effect of the structural parameters of aliphatic and aromatic carboxylic acids, dicarboxylic acids, their anhydrides, imides and nitro compounds on their inhibition efficiency for the corrosion of steel in hydrocarbon /electrolyte system.

According to Dinnappa and Mayanna, the corrosion inhibition of benzoic acid, p-toluic acid, p-nitro benzoic acid and terephthalic acid for Cu in perchloric acid is due to the adsorption of inhibitor molecules at the metal –solution interface. Bilgic and Yilmaz have reported that the inhibition efficiency of benzoic acid for steel corrosion in 0.5 M H₂SO₄ was found to increase by the addition of NaCl, NaBr and NaI. However potassium salts of the same halides are less effective than sodium salts.

Based on ATR and FTIR spectra, Frederic et al. have explained that the protection mechanism of cerium and lanthanum cinnamate based corrosion inhibitors on the corrosion of steel in neutral chloride solution is due to the adsorption of the rare earth metal cinnamate complex followed by the hydrolysis of the REM (Rare Earth Metal) to form a barrier oxide on the steel surface. Abd -El Kadher et al. have evaluated the corrosion inhibition effect of sodium benzoate, calcium gluconate and sodium glycerophosphate as co-inhibitors with sodium tungstate in distilled water and in 10⁻³ M NaCl. Tungstate –carboxylate
combinations have also been reported for corrosion and scale inhibition.\textsuperscript{97} A volatile rust prevention paper has been developed based on the synergistic effect of tungstate, hexamine and sodium benzoate, which can be used in rust prevention of steel, Al and Cu etc.\textsuperscript{98}

Nagaraju et al\textsuperscript{99} have studied the corrosion inhibition of potassium hydrogen phthalate, phthalic acid and salicylic acid on the corrosion of brass in sulphuric acid. Bilgic and Sahin\textsuperscript{100} have investigated the corrosion inhibition of steel by salicylic acid in acid media. A new inhibitor formulation with synergistic property containing cinnamate and substituted cinnamate with rare earth metals has been designed and they have been noted to perform better than benzoate anion.\textsuperscript{101}

Granata et al\textsuperscript{102} have studied the inhibitive action of many aromatic and aliphatic monocarboxylates and reported that carboxylates, oxidants and controlled pH yields corrosion free environment for steel in chloride containing aqueous solutions. Cinnamylidene acetate provides excellent protection for steel for a long period and it also controls crevice corrosion.

Stefanova\textsuperscript{103} has studied the inhibitor and biocidal efficiency of three chemical compounds – potassium permanganate, sodium benzoate and cetylpyridinium bromide (CPB) as additives to cooling water systems for corrosion protection of the metal equipment and against microbiological contamination. Phthalic anhydride, ATMP, zinc ions as a three components inhibitor has good adsorption and corrosion inhibiting properties.\textsuperscript{104} Adsorption of bromine labelled aromatic carboxylic acid corrosion inhibitor on iron polarized in the active region was studied with EQCM, EIS and XPS.\textsuperscript{105}

Pavlovi et al\textsuperscript{106} have studied the effect of benzoic acid on the corrosion and stabilization of electrodeposited copper powder. Eurof Davies and Slaiman\textsuperscript{107} have discussed the role of dissolved oxygen in decreasing the corrosion of iron by the inhibitor sodium benzoate.
II.5. Aliphatic Monocarboxylic acids and their Derivatives as corrosion inhibitors:

Szauer and Brandt\textsuperscript{108} have related the inhibition efficiency of amines and fatty acids for iron

- with the amount of complexes formed
- on the spatial and chemical structure of individual compounds and their complexes
- the adsorption forces involved and
- the interaction within the adsorption layer.

Lykov et al\textsuperscript{109} have reported that synthetic unsaturated fatty acids give good corrosion protection to carbon steel in jet fuels. Rocca and Steinmetz\textsuperscript{110} have evaluated the inhibition efficiency of sodium mono carboxylates in aqueous solutions for Pb using electrochemical methods and have shown that the longest carbon chain provides maximum efficiency and inhibition due to passivation of metals. Szauer has investigated the inhibition efficiency of salts of amines and unsaturated fatty acids present in organic coatings in acid\textsuperscript{111} and neutral media.\textsuperscript{112}

Lahodney and Popov\textsuperscript{113} have examined the inhibitive action of sodium gluconate and sodium tetra borate on mild steel using potentiodynamic polarization and weight–loss measurements and reported that the role of sodium tetra borate is to stabilize the protective film formed on the surface of mild steel. According to Szauer and Brandt\textsuperscript{114} the corrosion inhibition of iron by triethylamine salts of 18C unsaturated fatty acids in 0.5M deaerated H\textsubscript{2}SO\textsubscript{4} solutions is due to the preferential adsorption of fatty acids on the metal surface. The main role of amine is to cross-link the acid chains adsorbed on the iron surface.

Reinaldo Sim es Goncalves et al\textsuperscript{115} have studied the inhibitive action of acetate ions for the corrosion processes of low carbon steel in hydrated ethanol
by potentiodynamic, conductance and mass-loss measurements and reported that the anodic oxidation of electrode decreases with increase in the concentration of acetate ions. Singh and Singh\textsuperscript{116} have reported that copper metal exhibited active passive behaviour in the concentration range of 30-70 mol/o of acetic acid in the solution mixture containing both formic and acetic acid.

**II.6. Aliphatic Di and Tricarboxylic acids as corrosion inhibitors:**

Gunasekaran et al\textsuperscript{117} have established the synergistic effect of tartrate with organophosphonic acid and zinc metal ions in neutral environment on the corrosion inhibition of steel. Muthumani et al\textsuperscript{118} have examined the inhibition efficiency of sodium potassium tartrate in controlling the corrosion of carbon steel immersed in ground water in the absence and presence of Zn\textsuperscript{2+}. According to Baah & Baah\textsuperscript{119} the inhibition effect of oxalic acid on the corrosion of Cu in concentrated propionic acid and dil.citric acid is due to the formation of oxide layer on the surface of the sample. Shao et al\textsuperscript{120} reported that calcium ions form complex with tartrate ions and this complex acts as interface inhibitor for the corrosion of Al in an alkaline solution. Almeida and Giannetti\textsuperscript{121} have examined the protective film growth on tin in perchlorate and citric acid and reported that pitting inhibition may be due to the formation of the mixed layer of tin oxide and tin-citrate complex on the electrode surface.

Muller et al\textsuperscript{122} have reported that soluble zinc (II) Al(III) or cerium (III) chelates of citric acid exhibits excellent inhibiting effect for zinc pigments in aqueous alkaline media.

Singh and Archana\textsuperscript{123, 124} have studied the corrosion characteristics of Al alloys in oxalic acid. Giacomelli et al\textsuperscript{125} have reported that oxalic acid is found to be a good corrosion inhibitor for carbon steel in acid medium for pH greater than 3. Mercer and William\textsuperscript{126} have compared the corrosion inhibition of aliphatic dibasic acid such as 1,10-decanedioic acid and mono basic acid such as octanoic acid with the traditional inhibitor like benzoic acid in automotive cooling systems.
According to Giacomelli et al\textsuperscript{127} the inhibitive effect of succinic acid on the corrosion resistance of mild steel is due to the decrease in the anodic and cathodic reactions up to pH 3. Above pH 4, no inhibitive effect is observed. Sagoe et al\textsuperscript{128} have studied the corrosion inhibition of steel in concrete by malonic acid. The study report of Spathis et al\textsuperscript{129} on the corrosion and stress corrosion cracking behavior of Al alloy in acid medium, in the presence of various carboxylic acids (saturated or not, with different number of carboxylic, methyl or hydroxyl groups) has revealed that

- Malonic acid exhibits better protective property due to adsorption on the metal surface,
- Saturated dicarboxylic acid provides better protection against stress cracking corrosion,
- The presence of methyl group improves the protective property of the oxide.

Muller\textsuperscript{130} has reported that the corrosion inhibition of Al pigment in aqueous alkaline medium by citric acid is due to the

i) Formation of aluminium- citrate complex

ii) Agaric acid, a surfactant inhibits the corrosion of Al pigments better than citric acid. Abd El- Maksoud et al\textsuperscript{131} have examined the electrochemical behaviour of carbon steel in a wide range of concentration of gluconate and tartrate by potentiodynamic and open circuit measurements and reported that corrosivity of carbon steel in tartrate is higher than in gluconate. Pemberton et al\textsuperscript{132} have observed a synergistic effect between sodium sebaccate and benzotriazole for the corrosion inhibition of cast iron, galvanized steel and mild steel in distilled water and dilute salt solutions.
Butler and Mercer\textsuperscript{133} have reported that disodium sebaccate when used with benzotriazole provides effective inhibition of the corrosion of carbon steel, cast iron, Al alloy, Pb and tin solder, Cu and brass in engine coolants containing 50% ethanediol. Beale et al\textsuperscript{134} have evaluated a novel engine coolant formulations containing ethanediol, disodium sebaccate and benzotriazole. John Amal Raj et al\textsuperscript{135,136} have reported the influence of dihydroxy dicarboxylic acid on the inhibition efficiency of a phophonate-Zn\textsuperscript{2+} system in controlling the corrosion of carbon steel in an aqueous environment containing Cl\textsuperscript{-} ion. Thangavelu et al\textsuperscript{137} have evaluated the synergistic effect of citrate and Zn\textsuperscript{2+} on the corrosion of carbon in dil. salt solutions.

Dong-Jin Choi et al\textsuperscript{138} have reported that the new all-organic multicomponent inhibitor blend composed of citric acid/phosphonates/acrylate copolymer/ isothiazolone effectively decreases the corrosion, scale built up and microbial growth for carbon steel in open recirculating cooling water system. It is reported that the inhibition effect are due to the formation of a protective film. Ruba Helen Florence et al\textsuperscript{139} have studied the corrosion inhibition of carbon steel in ground water by adipic acid and Zn\textsuperscript{2+} system.

Felicia Rajammal Selvarani et al\textsuperscript{140} have reported the existence of synergism between succinic acid and Zn\textsuperscript{2+} in controlling the corrosion of carbon steel in well water. Arichandran et al\textsuperscript{141} have reported that the protective film formed on the carbon steel immersed in well water containing citrate-Zn\textsuperscript{2+} system consists of iron –citrate complex and Zn(OH)\textsubscript{2}.Vigant et al\textsuperscript{142} have observed that alkenyl succinic acid, calcium alkyl benzolsulphonate, urea and alkyl succinimide replaces, displaces HBr, HCl, H\textsubscript{2}SO\textsubscript{4} and acetic acid which are found on the surface of the steel in industrial and sea atmospheres and provide protection due to chemical or physical adsorption.

The influence of the inhibitive system consisting of ATMP, oxalic acid or phthalic anhydride and zinc sulphate on the rate of corrosion of steel in simulated
industrial water of variable chemical composition and in water being chlorinated has been studied by gravimetric method. This formulation is considered as a perspective inhibitor for the corrosion protection of industrial cooling and heating water installation.\textsuperscript{143} Kubicki et al\textsuperscript{144} have investigated the inhibitive property of amino(trimethylene phosphoric acid) (ATMP) in preventing the corrosion of iron in neutral, aqueous solution in combination with carboxylic acid and Zn\textsuperscript{2+} salts. Greatest protective effectiveness was obtained for tricomponent composition containing ATMP, phthalic acid or oxalic acid and Zn\textsuperscript{2+}. Sodium dodecyl succinate and sodium nitrite show synergistic effect in controlling the corrosion of steel in simulated cooling water circulates\textsuperscript{145}

**II.7. Zinc ions as corrosion inhibitors:**

Zinc ions have long been considered as valuable corrosion inhibitors for carbon steel in aerated water because of the protection afforded by a cathodic polarization mechanism.\textsuperscript{146,147} However due to the problem of toxicity of Zn\textsuperscript{2+} ions, it is necessary to reduce the concentration of Zn\textsuperscript{2+} by introducing a synergist which is environmentally friendly. Several organic inhibitors were evaluated as excellent co-inhibitors with Zn\textsuperscript{2+} for carbon steel substrate. According to Pech and Bartolo\textsuperscript{19} the inhibitive effect of N-phosphonomethyl glycine-Zn\textsuperscript{2+} mixture on corrosion of steel in neutral medium is due to the retardation of anodic and cathodic process due to the film Fe- inhibitor complex and ZnO. Amino carboxylic acids and their N-phosphonomethyl derivatives with or without additives (Zn or metavanadate ion) have been studied in neutral solution by Kalman et al.\textsuperscript{22}

Gunasekaran et al\textsuperscript{117} have established the synergistic effect of tartrate with organophosphonic acid and zinc metal ions in neutral environment on the corrosion of steel. Muthumani et al\textsuperscript{118} have examined the inhibition efficiency of sodium potassium tartrate in controlling the corrosion of carbon steel immersed in ground water in the absence and presence of Zn\textsuperscript{2+}. John Amal Raj et al\textsuperscript{135,136}
have reported the synergistic effect of dihydroxy dicarboxylic acid on the inhibition efficiency of a phophonate-Zn\(^{2+}\) system in controlling the corrosion of carbon steel in an aqueous environment containing Cl\(^{-}\) ion.

Thangavelu et al\(^{137}\) have evaluated the synergistic effect of citrate and Zn\(^{2+}\) on the corrosion of carbon in dil.salt solutions. Ruba Helen Florence et al\(^{139}\) have studied the corrosion inhibition of carbon steel in groundwater by adipic acid and Zn\(^{2+}\) system. Felicia Rajammal Selvarani et al\(^{140}\) have reported the existence of synergism between Succinic acid and Zn\(^{2+}\) in controlling corrosion of carbon steel in well water. Aarichandran et al\(^{141}\) have reported that the protective film formed on the carbon steel immersed in well water containing citrate-Zn\(^{2+}\) system consists of iron–citrate complex and Zn(OH)\(_2\). The influence of the inhibitive system consisting of ATMP, oxalic acid or phthalic anhydride and zinc sulphate on the rate of corrosion of steel in simulated industrial water of variable chemical composition and in water being chlorinated has been studied by gravimetric method. This formulation is considered as a perspective inhibitor for the corrosion protection of industrial cooling and heating water installation.\(^{143}\) Kubicki et al\(^{144}\) have investigated the inhibitive property of amino(trimethylene phosphoric acid) (ATMP) in preventing the corrosion of iron in neutral, aqueous solution in combination with carboxylic acid and Zn\(^{2+}\) salts. Greatest protective effectiveness was obtained for tricomponent composition containing ATMP, phthalic acid or oxalic acid and Zn\(^{2+}\). Susai Rajendran et al have studied the role of Zn\(^{2+}\) in the inhibition of corrosion of mild steel in neutral, aqueous environment, containing 60 ppm of Cl\(^{-}\) by the inhibitors-molybdate,\(^{148}\) HEDP\(^{149}\) and HEDP-molybdate.\(^{150}\) Rajendran et al\(^{151}\) have reported that phenylphosphonate acts synergistically with low concentration of Zn\(^{2+}\) in inhibiting the corrosion of mild steel in a neutral aqueous chloride environment. However at higher concentrations of Zn\(^{2+}\) decrease in inhibition efficiency is observed due to the formation of a insoluble Zn\(^{2+}\)-PPA complex The presence of Zn\(^{2+}\) ions facilitate the transport of these inhibitors from the bulk to the metal.
surface. Both cathodic and anodic reactions are controlled. Corrosion of iron-based alloys in a circulating water is decreased by a synergistic inhibitor mixture containing HEDP, hydroxy phosphonoacetic acid and sodium tolyltriazole. 2-phosphonobutane-1, 2,4-tricarboxylic acid (pBTCA) shows synergistic effect with Zn$^{2+}$ ions, Zn$^{2+}$-HEDP combination and MnCl$_2$.4H$_2$O. When pBTCA is used along with Zn$^{2+}$ in the corrosion inhibition of mild steel in tap water, Zn(Ca)-PBTCA-Fe(III) sequestering film deposited on the surface of mild steel inhibits corrosion effectively.

Yang Zhang et al have reported that iminodimethylene phosphonic acid when used in combination with Zn$^{2+}$ and polyacrylate shows synergistic effect and act as multifunctional inhibitor for cooling water. Venugopalan et al have developed the inhibitor formulation consisting of zinc ions, HEDP and an organic additive zinc gluconate for corrosion inhibition of mild steel in neutral aqueous medium containing 60 ppm of Cl$^-$ ions. It is reported that it acts as a mixed inhibitor. Complexes of HEDP and gluconate ions and Zn(OH)$_2$ were found on the metal surface.

Studies on ascorbate as second synergist along with Zn$^{2+}$ and phosphonates in the corrosion inhibition of carbon steel in low chloride environment were reported by Apparao and Srinivas Rao. Wrubl et al have appraised the efficiency of Zn basic gluconate as a corrosion inhibitor for mild steel in sodium chloride solution. According to them, the inhibition is due to Zn$^{2+}$ ions, Zn(C$_6$H$_{11}$O$_7$)$^+$ and (C$_6$H$_{11}$O$_7$)$^-$ ion. Susai Rajendran et al have reported the synergistic and antagonistic effect existing among polyacrylamide, phenyl phosphonates and Zn$^{2+}$ on the inhibition of corrosion of mild steel in an aqueous neutral environment. Meena et al have investigated the influence of Zn$^{2+}$ on the corrosion rate of carbon steel immersed in an aqueous environment containing 60 ppm of Cl$^-$ and carboxymethyl cellulose (CMC). A synergistic effect is noticed between CMC and Zn$^{2+}$. Manjula et al have studied the corrosion behavior of carbon steel in aqueous medium in the presence of
N-cetyl-N,N,N-trimethyl ammonium bromide (CTAB), Zn$^{2+}$ and calcium gluconate.

The existence of synergism between molybdate and Zn$^{2+}$ ions has been reported$^{163-166}$. Corrosion inhibition efficiency of HEDP synergistically was improved by adding Zn$^{2+}$ ions$^{165,167-169}$. The synergistic effect of Zn$^{2+}$ and HEDP in decreasing the corrosion rates of steel in seawater was observed$^{168}$. The protective cathodic film on the steel consists of Mg (predominant), P and Zn. Gonzales et al$^{170}$ have carried out electrochemical measurements and used analytical techniques (XPS, Reflection absorption spectroscopy) to investigate the inhibition of corrosion of carbon steel by a mixture of zinc salt and phosphonic acid. They have reported the formation of a homogeneous thin film on the surface of the metal.

**II.8. Biocides**

Cooling water systems are extremely vulnerable to microbial contamination. Problems occur when microbes begin to proliferate and attach to system surfaces. For example, in the case of cooling coil systems microbes can easily congest the system, restricting water flow and ultimately, reduce heat exchange. The result is increased operating costs in the form of poor heat dissipation, overall system inefficiency, and system clean up, including any downtime that may be necessary. Corrosion can also result from unchecked microbial growth. Microorganisms such as bacteria, fungi and algae can combine with organic compounds to form biofilms. The microbes in these films produce products of metabolism that are corrosive in nature. The result is pitting and corrosion of metal components. Wooden system support structures are also vulnerable, as wood-destroying fungi can cause significant damage as well.
To eliminate the threat of such potential problems and achieve optimum system efficiency, microbiological activity within a system must be properly controlled. Though a seemingly straightforward goal, cost concerns, system operating guidelines, and additive compatibility all greatly influence treatment choice. Environmental, health and safety considerations also have a great impact. To be considered a viable option, a biocide must successfully control a broad spectrum of microbial contamination, provide cost-effective performance and prove compatible with other system components, while at the same time meeting stringent environmental, health and safety standards. Literature survey has shown a number of biocides which were used along with corrosion inhibitors.

Ramesh et al\textsuperscript{171} have investigated the inhibition efficiency of triazolephosphonates compounds namely 3-benzyledene-amino-1,2,4-triazolephosphonates, 3-cinnamyledene-amino-1,2,4-triazolephosphonates and 3-anisalidene-amino-1,2,4-triazolephosphonates, along with biocide action on corrosion of mild steel. They have also evaluated the biocidal action of the inhibitors on the corrosion control of Cu\textsuperscript{172} in neutral aqueous environment. Stefanova\textsuperscript{103} has studied the biocidal efficiency of cetylpyridinium bromide, (CPB), potassium permanganate and sodium benzoate. He has reported that the CPB has a wide range of effect for microorganisms typical for water media. Its high biocide efficiency is a prerequisite for its use as additive to cooling water. Sodium benzoate and potassium permanganate acts selectively to particular representative of the microorganism’s characteristic for the water media.

Dong-Jin Choi et al\textsuperscript{138} have reported that the new all-organic inhibitor blend composed of citric acid/phosphonates/acrylate copolymer/ isothiazolone effectively decreases the corrosion, scale built up and microbial growth for carbon steel in open recirculating cooling water system. It is reported that the inhibition effect are due to the formation of a protective film. Rajendran et al\textsuperscript{173-175} have studied the influence of biocide on corrosion inhibition of mild steel by ATMP-Zn\textsuperscript{2+} system. The formulation consisting of 200 ppm of ATMP,
100 ppm CTAB has shown 99% corrosion inhibition efficiency and 100% biocidal efficiency. It is reported that CTAB acts as an excellent biocide as monomer and also as micelle\textsuperscript{176}. Bernard et al\textsuperscript{177} have evaluated the bacterial efficiencies of the four bacteriocides – organosulphur, mixed aldehyde-organo sulphur, mixed aldehyde-quaternary ammonium and organo brome compounds on the polluted water from sulphuric acid manufacturing plants. Manimegalai et al\textsuperscript{178} have examined the inhibitive property as well as the biocidal properties of the leaf extracts of Azadiracta Indica and reported that the inhibitor has very effective biocidal property as well as inhibitive property for mild steel in fresh water environment. It is reported that most of the biofilms are sensitive to the detergent biocide SDS\textsuperscript{179,180}.

Iwalokun et al\textsuperscript{181} have suggested to use urea and SDS in the laboratory to reduce the risk of infection with virulent proteus strains. Richard et al\textsuperscript{182} have investigated the effect of the surfactants alcohol ethoxylates, amine ethoxylates, amine oxide and SDS on bacterial cell membranes using EPR spectroscopy.

Lin et al\textsuperscript{183} have reported that CPC a quaternary ammonium salt and a cationic surfactant has been used as a biocide in personal hygiene products. It is reported that CPC acts as an antifungal agent\textsuperscript{184} and as a biocide\textsuperscript{251} for cosmetics, toiletries and pharmaceuticals activity.

**II.9. Biocides as corrosion inhibitors:**

The major problems in industrial use of the cooling water system are corrosion of the metal equipment, contamination of the circulating water system with microorganisms, and deposit formation that worsens the heat exchange. To solve the above problems complex treatment of the water is required including the use of the metal corrosion and antideposit additives. In view of the large water losses in the systems resulting from evaporation and leakages, the application of these chemicals, which are economically expedient, if they behave efficiently at low concentrations are sought. The compatibility of the different
additives in the system also matters as very often a good biocide exhibits strong corrosion effect on the metal equipment and reduces the effect of inhibitors used, that is why it is of interest to find out chemical compounds which when added to water will have more than one function or at least will not negatively affect the action of the other additives.

Many surfactants function as biocides. Several surfactants have also been used as corrosion inhibitors.\textsuperscript{186-190} Review of literature reveals that sodium dodecyl sulphate and many quaternary ammonium salts such as CTAB and CPC functions as excellent corrosion inhibitors in different environment for various metals. According to Bereket and Yurt\textsuperscript{191} quaternary ammonium salts behave as mixed inhibitors on the corrosion of low carbon steel in acidic solutions and the inhibition efficiency is maximum around and above the critical micellar concentrations.

The studies on the corrosion inhibition of iron in acidic solutions by alkyl quaternary ammonium halides by Lin Niu et al\textsuperscript{192} reveal that the structure of alkyl group and the type of halide ions of these inhibitors greatly influence the inhibition efficiency. Saeed and Ali\textsuperscript{193} have synthesized a variety of bisquaternary ammonium salts and they exhibit excellent inhibition for the corrosion of carbon steel. Bernard et al\textsuperscript{194} have reported that the inhibition efficiency increases with increase in the polar head group size and also the length of the carbon chain of quaternary ammonium salts due to the formation of a close packed layer. According to Hoar and Holliday\textsuperscript{195}, the inhibiting action of CTAB is due to the adsorption of cetyl ammonium cations on the most active anodic sites, which interfere with the anodic reactions by hindering the escape of Fe\textsuperscript{2+} ions from the metal surface into the solution. Rajendran et al have investigated the influence of the cationic surfactant N-cetyl,N,N,N-trimethyl ammonium bromide (CTAB) on the Zn\textsuperscript{2+}-ATMP\textsuperscript{174}, Zn\textsuperscript{2+}-HEDP\textsuperscript{175} and the calcium gluconate-Zn\textsuperscript{2+} \textsuperscript{196} in controlling the corrosion of carbon steel in aqueous environment. Manjula et al\textsuperscript{197} have studied the corrosion behaviour of carbon
steel in the presence of N-cetyl, N,N,N-trimethylammonium bromide, Zn$^{2+}$ and calcium gluconate. Houyi Ma et al\textsuperscript{198} have investigated the inhibitive action of CTAB, SDS, sodium oleate and polyoxyethylene sorbitan monooleate on the corrosion behaviour of Cu by electron impedance spectroscopy. CTAB was found to be the most efficient inhibitor due to the synergistic effect between bromide anions and the positive quaternary ammonium ions. Karpagavalli and Rajeswari\textsuperscript{199} have reported the application of CTAB as inhibitor for the corrosion of brass in ground water. Soror and El-Ziady\textsuperscript{200} have studied the effect of CTAB on the corrosion of carbon steel in acid. Lalitha et al\textsuperscript{201} have shown the existence of synergistic effect between SDS, CTAB with triazoles for the corrosion inhibitions of copper in acid medium. Michael.L.Free\textsuperscript{202} has related the corrosion inhibition of mild steel in acidic medium by surfactant molecules cetyl pyridinium chloride and cetyltrimethylammonium bromide to the surfactant’s ability to aggregate at interfaces and in solution. Lin Wang et al\textsuperscript{203} have shown that both 2-mercaptothiazoline and cetylpyridinium chloride functions as effective inhibitors for low carbon steel over a wide concentration range of aqueous phosphoric acid solution.

According to Abd-El-Maksoud\textsuperscript{204} hexadecylpyridinium bromide and hexadecyltrimethyl ammonium bromide, act as mixed inhibitors for iron and Cu in HCl and H$_2$SO$_4$ due to the potential of the zero charge of the metal and due to the adsorption ability of chloride and sulfate ions on the metal surfaces.

Suguna et al\textsuperscript{205} have determined the corrosion rates of carbon steel in the absence and presence of sodium dodecyl sulfate and Zn$^{2+}$ in aqueous solutions. Rong Guo et al\textsuperscript{206} have studied the effects of sodium dodecyl sulphate (SDS) and some alcohols (ethanol/n-butanol) on the inhibition of the corrosion of Ni. Abd-El-Rehim et al\textsuperscript{207} have reported that the inhibition of corrosion of Al alloy in 1 M HCl in the temperature range 10-60 C occurs through the adsorption of the anionic surfactant SDS on the metal surface without modifying the mechanism of the corrosion process. The effect of SDS and Cu corrosion has been studied in
the absence and presence of benzotriazole using electrochemical impedance and surface tension measurements.\textsuperscript{208\textendash}209 Susai Rajendran et al\textsuperscript{210} have evaluated the inhibition efficiency of SDS in controlling the corrosion of carbon steel immersed in 60 ppm of NaCl in the absence and presence of Zn$^{2+}$. FTIR spectrum has revealed the presence of a film containing iron-SDS complex and Zn(OH)$_2$.

Monticelli et al\textsuperscript{211} have investigated the corrosion inhibition of Al alloy (AA 6351) in 0.01 M NaCl using inhibitors such as sodium salts of N-dodecanoyl-N-methylglycine (NLS), dodecyl sulfate (LS), N-dodecanoyl-N-methyltaurine (NLT) and dodecylbenzene sulfonate (DBS).

The existence of synergism and antagonism in mild steel corrosion inhibition by sodium dodecylbenzene sulfonate and hexamethylenetetramine has been ascribed to the formation of hemi-micellar aggregation that provoke inhibitor desorption from the metal/solution interface at higher concentration.\textsuperscript{212}

Susai Rajendran et al\textsuperscript{213} have reported the mutual influence of HEDP and SDS on the corrosion inhibition of carbon steel immersed in rain water in the presence of Zn$^{2+}$. Rajendran et al\textsuperscript{214} have studied the influence of sodium sulfate, SDS, pH and duration of immersion on the inhibition efficiency of polyvinyl alcohol –Zn$^{2+}$ system. They have noted the existence of synergistic effect between PVA–Zn$^{2+}$ and SDS.

The literature survey suggests that corrosion inhibitors based on carboxylic acids remain a fruitful field of investigation. Literature survey also clearly has shown the importance of Zn$^{2+}$ ions as corrosion inhibitor. Zn$^{2+}$ was also successfully employed as a co-inhibitor with many organic inhibitors. In this context, the objective of the present set of studies was framed to investigate in detail, the mutual influence of Zn$^{2+}$ and few dicarboxylic acids using different techniques under different experimental conditions and the compatibility of the inhibitor systems with few biocides.
II.10. BIBLIOGRAPHY


2. E.V. Bogatyreva and V.V. Nagaev, Zh Prikl Khim, 35 (1962) 556.

3. E.V. Bogatyreva, Khim Khim Tekhnol (1) (1959)


6. N.G. Klyuchnikov and N.S. Novoshinskaya, Zh Prikl Khim, 36 (1963) 2470


11. Chemistry research for the years 1958, 1951 and 1954 Published by HMSO, London.


176. S. Rajendran, R. M. Joany and N. Palaniswamy, Tenth National Cong. on Corrosion Control, Madurai, Organised by NCCI, Karaikudi, 6-8 Sep. (2000) 251-261


180. www.ibt.dtu.dk/im/mme/pdf/Hentzer-2002-1


184. www.patentstorm.us/class/424/413- Cellulosic _material_or_ building_material.html.

185. infochems.com/chemdb/product_list.


