

Part III

Corrosion inhibition studies

Chapter 1

Nimmy Kuriakose “Physicochemical, thermoanalytical, electrochemical and antitumour studies of transition metal complexes of schiff bases derived from heterocyclic carbonyl compounds” Thesis. Department of Chemistry, St. Thomas College, University of Calicut, 2015

CHAPTER 1

INTRODUCTION AND REVIEW

Corrosion is the gradual destruction or disintegration of metal by chemical or electrochemical reaction with their environment. It involves the electrochemical oxidation of metals in the presence of an oxidant such as oxygen. A well known example of electrochemical corrosion is rusting, which involves the formation of iron oxides. Corrosion of metals typically produces oxide or salt of the original metal¹. Not only metals, materials such as ceramics or polymers are also vulnerable to corrosion. Corrosion can cause degradation in the useful properties of materials such as strength, appearance and permeability to liquids and gases.

Many metals corrode merely from exposure to moisture in air, but the process can be accelerated by the presence of certain substances. It is observed that corrosion is concentrated locally in the form a pit or crack, and in some cases it is extended across a wide area more or less uniformly. The thermodynamic or chemical energy¹ stored in a metal or that is freed by its corrosion varies from metal to metal. For example, the most common iron ore hematite is an oxide of iron. The most common product of the corrosion of iron, rust, has a similar chemical composition and colour. The energy required to convert iron ore to metallic iron is returned when the iron corrodes to form the original compound, only the rate of energy change is different¹. Metals such as iron, magnesium and



aluminum have higher and metals such as copper, silver and gold have relatively lower energy.

Economic impact of corrosion

The direct cost associated with metallic corrosion in the US industry was reported as around \$280 billion in 2002, by the US Federal Highway Administration². It is reported that rust is one of the most common causes of bridge accidents. The collapse of the Mianus river bridge in 1983 was due to the corrosion of the bearings which resulted in the death of three drivers on the roadway at the time. In West Virginia, the Silver bridge which was a steel suspension bridge collapsed within a minute, killing 46 people on the bridge at the time. Here also the rust was the reason. The corrosion of concrete covered steel and iron causes severe structural problems. As rust has a much higher volume than the originating mass of iron, its build-up can also cause failure by forcing apart adjacent parts. The corrosion spots must be detected before the total destruction of the concrete structure by measuring half-cell potential.

Protection from corrosion

Some metals are more intrinsically resistant to corrosion than others. Application of water and oil based corrosion inhibitors can prevent the oxidation and the formation of rust on metal surfaces. There are various ways of protection of metals from corrosion.

Surface coatings: Anticorrosion methods like plating, painting and the application of enamel provide a barrier between the metal surface and the damaging environment. Plating with more noble materials than the substrate is very effective. For example, chromium or zinc can be plated on steel. Painting either by roller or brush is more desirable for tight spaces; spray would be better for larger coating areas such as steel

decks and waterfront applications². A slip resistant coating with polyurethane, like Durabak-M26, can act as an anti-corrosive membrane. Although coatings are relatively easy to apply, temperature and humidity can affect dryness and durability of the coatings.

Reactive coatings: The electrochemical reactions on surfaces can be prevented by coating corrosion inhibitor chemicals which form an electrically insulating or chemically impermeable coating on the exposed areas. Chemicals like chromates, phosphates, salts in hard water, polyaniline, other conducting polymers and a wide range of long chain organic molecules with ionic end groups which resemble surfactants can be used. The advantage of this method is that it makes the system less sensitive to scratches or defects in the coating and there is possibility of adding extra inhibitors whenever the surface gets exposed.

Anodization: Anodizing is very resilient to weathering and corrosion, so it is commonly used for buildings and other areas where the surface will come into regular contact with the corroding environments. But failure in frequent cleaning will end with panel edge staining.

Bio-film coatings: The application of certain species of bacterial films on the surface of metals in highly corrosive environments is a new method of corrosion inhibition. The corrosion resistance is increased outstandingly in this process. Interestingly, it is reported that mild steel corrosion from sulfate-reducing bacteria can be inhibited by an antimicrobial biofilms³.

Controlled permeability formwork (CPF): It is a method of preventing the corrosion of reinforcement by naturally enhancing the durability of the cover during concrete

placement. The effects of carbonation, chlorides, frost and abrasion can be reduced with this method³.

Cathodic protection: Here the corrosion of a metal surface is prevented by making the surface as cathode of an electrochemical cell. Steel, fuel pipelines, tanks, ships, steel pier piles and offshore oil platforms are often protected in this way.

Anodic protection: An anodic current is impressed on the metal structure to be protected.. This method is employed in aggressive environments, like sulfuric acid. Materials like stainless steel that exhibit passivity are protected in this way.

Impressed current cathodic protection: This system use anodes connected to a DC power source. Anodes for ICCP systems are tubular and solid rod shapes of various specialized materials. These include high silicon cast iron, graphite, mixed metal oxide or platinum coated titanium or niobium coated rod and wires⁴.

Corrosion inhibitors: This is an important method of prevention of corrosion especially in hydrochloric acid and sulphuric acid solutions which are used for the pickling of aluminium and electrochemical etching. The corrosion inhibitors decrease the rate of metal dissolution in acid solutions. They usually include organic compounds of nitrogen. The effect of such organic compounds on the corrosion behaviour of iron and steel in acidic solutions are studied and these compounds are characterised by their rapid action⁴.

The inhibitory action of organic corrosion inhibitors is due to the adsorption of molecules on the metal-solution interface. Four distinct mechanisms are believed to occur⁵, (1) electrostatic attraction between the metal and charged molecules (2) interaction between uncharged electron pairs in the inhibitor and the metal (3) interaction between the metal and the p-electrons of the inhibitor and (4) a combination of

mechanism (1) and (3). If the inhibitor molecule has greater tendency to form stronger coordination bonds with the metal, the inhibition efficiency is increased. Usually phosphorus containing molecule is found to have the strongest tendency to prevent corrosion followed by sulphur, nitrogen and oxygen⁶. The presence of lone pairs of electrons on N, O and S atoms contribute to their structural features that results in the adsorption of these molecules on the metal surface^{7,8}. Generally the efficiency of the organic inhibitor compounds incorporating hetero atoms like O, N, S and in some cases Se and P are reported as very efficient corrosion inhibitors⁹⁻¹¹. The efficiency of these compounds depends upon electron density present around the hetero atoms and the number of adsorption sites on the surfaces¹². Moreover, the charge density and molecular size of the compounds also play important roles¹³⁻¹⁸. The mode of adsorption and formation of metallic complexes determines the activity and efficiency of the inhibitor molecules¹⁹. The capacity of hetero atoms to form coordinate-covalent bond with metal is highlighted in their activity. Compounds having π -bonds also can exhibit good inhibitive properties due to interaction of π -orbital with metal surface²⁰. When both the above features combine, enhanced inhibition can be observed²¹⁻²³.

Literature search established that benzotriazoles and their derivatives, quinoline and benzaldehyde derivatives, alkaloids, quaternary imidazoline derivative, quaternary salts of benzenethiol, pyridine bases, triazoles, thiourea, imidazole azo derivatives, derivatives of toluidenes and chloroanilines etc possess marked inhibitory action²⁴⁻²⁹.

Schiff bases as corrosion inhibitors

The Schiff bases are compounds containing azomethine (C=N) linkage. These compounds are cheap and are characterized by high effectiveness and easy applications.

Ashish Kumar Singh et. al. reported that the corrosion inhibition effect of three Schiff base compounds namely, ethylenediamine bis-isatin (EDBI), hexane 1,4-diamine bis-isatin (HDBI) and thiocarbohydrazide bis-isatin (TCBI) were studied by gravimetric, potentiodynamic polarization, electrochemical impedance spectroscopy, atomic force microscopy and scanning electron microscopy³⁰. Adsorption of these inhibitors was according to the Frumkin isotherm. It was found that efficiency order followed by these inhibitors is TCBI>EDBI>HDBI. They reached into the conclusion that an efficient corrosion inhibitor molecule must have large size, planarity, unoccupied d-orbital and also an extensive number of π -electrons.

The corrosion inhibition effect of some Schiff bases N,N'-bis(2-hydroxybenzylidene)-1,3-diaminobenzene, N,N'-bis(4-bromobenzylidene)-1,3-diamino benzene and N,N'-bis(2-hydroxy-5-bromobenzylidene)-1,3-diaminobenzene was investigated on aluminium alloy in 0.5M HCl acid by M. T. Muniandy et. al.³¹. Weight loss measurements, potentiodynamic polarization studies and scanning electron microscopic (SEM) analysis showed that the inhibition ability of these Schiff bases are almost similar in acid medium. The potentiodynamic polarization studies revealed that, all the Schiff bases are mixed type inhibitors with a predominantly cathodic action. The inhibition efficiencies were found to increase linearly with inhibitor concentration. The inhibitor molecules obeyed Langmuir adsorption isotherm on aluminium surface. The formation of a protective layer on the metal surface was revealed by SEM studies. The inhibition

performance depends strongly on the type of functional groups substituted on the benzene ring.

M.D. Shah et. al. investigated the inhibition activity of trisalicylidene and tribenzylidene derivatives of triethylenetetramine on zinc metal in HCl medium³². 96-100% of inhibition efficiency was observed by the inhibitors at 1% concentrations in 0.5M and 1.0M HCl solutions. The efficiency of the former Schiff base was decreased after 120 minutes when temperature was increased from 35 to 65 °C while that of the other inhibitor remains almost constant 99.7%. The activation energies of corrosion were higher in the presence of inhibitors than in the blank. The spontaneity of adsorption of the inhibitor on the metal surface was evident from the negative values of heat of adsorption and free energy of adsorption. Cathodic polarization was found to be predominant in electrochemical studies. It was also suggested that Langmuir isotherm was obeyed on both anodic and cathodic sites.

The corrosion inhibition efficiencies of N, N'-bis (salicylidene)-1, 4-diaminophenylene (SDP) and N, N'-bis (3-methoxy salicylidene)-1, 4 diaminophenylene (MSDP) on an alloy (AA6061) in 1M hydrochloric acid were evaluated by weight loss method and scanning electron microscopic technique by S.P. Fakrudeen et. al.³³. The gravimetric study showed that the inhibition efficiency of these Schiff bases increases with increase in concentration and vary with solution temperature and immersion time. The mechanism of corrosion inhibition was postulated based on the thermodynamic parameters. The adsorption of molecules on the alloy surfaces obeyed Freundlich isotherm.

S. Thirugnanaselv et. al.³⁴ have reported that the corrosion inhibition efficiency of the Schiff base (4Z)-4-(3-phenylallylideneamino)-3-hydroxy naphthalene-1-sulfonic acid

(AC) on AZ31 magnesium alloy corrosion in 0.05mol/L HCl was studied by using weight loss method, electrochemical impedance spectroscopy and potentiodynamic polarization techniques. It is found that the Schiff base AC inhibited both anodic and cathodic reactions at all concentrations, and thus acting as a mixed type inhibitor, which is evident from the potentiodynamic polarization curves. The EIS measurements indicate that the polarization resistance increases as the additive concentration is increased, which may be attributed to the decrease in double layer capacitance. Langmuir adsorption isotherm was obeyed by the adsorption of AC molecules on the AZ31 magnesium alloy surface in 0.05mol/L HCl.

Vidhi Panchal et. al. investigated the effect of some newly synthesized Schiff bases namely o-chloroaniline-N-(p-methoxybenzylidene) and p-chloroaniline-N-(p-methoxybenzylidene) on Al-Mg alloy in 2 M HCl. Methods of study involved weight loss, galvanostatic polarization and EIS measurements³⁵. It is concluded that the percentage of inhibition efficiency was enhanced with inhibitor concentration and diminished with hike in temperature. The inhibition mechanism of the Schiff bases was postulated based on thermodynamic parameters and activation energy values. The inhibitors were found to adsorb on the metal surface according to the Langmuir isotherm. The results of polarization studies showed that these Schiff bases act as mixed type, but the cathode was more preferentially polarized.

Schiff bases as corrosion inhibitors on mild steel

Mild steel is an important metal regarding to its wide applications in industry in various mechanical and structural purposes. Being widely used in engineering fabrications it is much prone to corrosion by different corrosion agents of which

dangerous acids like HCl and H₂SO₄ are most common. HCl and H₂SO₄ have been used for drilling operations, pickling baths and in descaling processes.

Corrosion of mild steel and its alloys in different acid media has been extensively studied. The pH of solution, dissolved oxygen and temperature affect the rate of corrosion. It is adversely affected in the pH range 4 to 10 but fairly resistant to attack by alkali. Organic compounds bearing hetero atoms are found to be very effective as corrosion inhibitors for mild steel. Many investigators have explored the effect of some nitrogen containing compounds on corrosion of mild steel in different acid media.

Fatemeh baghaei³⁶ studied the inhibition effect of a newly synthesized Schiff base, namely 4-nitro-2-methoxy phenyl-N-salicylidine on mild steel in 0.5M HCl acid using electrochemical impedance spectroscopy (EIS), Tafel polarization and weight loss measurements. The inhibition efficiencies were found to increase with increase in the Schiff base concentration. Tafel polarization studies proved that the Schiff base have a mixed type inhibitory nature. The adsorption studies of this compound on a mild steel surface revealed that Langmuir adsorption isotherm was obeyed by the molecule and thermodynamic parameters proved that adsorption of inhibitor was of physical in nature.

Ashassi and co-workers³⁷ employed electrochemical and weight loss measurements to study the anticorrosive property of (4-chloro-benzylidene)-pyridine-2-yl-amine, benzylidene-pyridine-2-yl-amine and (4-benzylidene)-pyridine-2-yl-amine at 25⁰C in hydrochloric acid medium. The inhibition performance was found to be changed with the concentration and presence of substituent on the benzene ring. Langmuir adsorption isotherm was followed during the process. Polarization curves revealed that the Schiff bases were acting as mixed type inhibitors. The inhibition efficiency increased

as the inhibitor concentration increased.. Temperature studies were conducted in 25–43⁰C range. The energy of activation and thermodynamic parameters were also calculated. The high degree of correlation between the inhibition efficiency and parameters from QSAR models suggested that these compounds are good corrosion inhibitors.

T. Sethi et. al. conducted weight loss and thermometric methods to study the corrosion inhibition of mild steel in hydrochloric acid and sulphuric acid solutions by Schiff bases N-(4-N,N-dimethylaminobenzal)-p-anisidine, N-(4-N,N-dimethylamino benzal)-p-toluidine and N-(4-N,N-dimethylaminobenzal)-2,4-dinitroaniline³⁸. The inhibition efficiencies were found to be dependent on both the concentrations of inhibitors and the acids. The Schiff bases exhibited better inhibition efficiency in HCl rather than in sulphuric acid. Maximum inhibition efficiency observed was 95.55% for mild steel in HCl solution. The inhibition efficiencies of the Schiff bases when compared with that of their parent amines proved that the presence of azomethine linkage substantially increases the inhibition property. Also it was found that inhibition efficiency of all amines increases with concentration and decreases with increasing concentration of the acids.

Mass loss and thermometric methods were used to study the corrosion inhibitory effect of synthesised Schiff's bases, N-(furfurilidene)-4-methoxyaniline (SB1), N-(furfurilidene)-4-methylaniline (SB2), N-(salicylidene)-4-methoxyaniline (SB3), N-(cinnamalidene)-4-methoxyaniline (SB4) and N-(cinnamalidene)-2-methylaniline (SB5) on mild steel in sulphuric acid solutions by Upadhyay et. al.³⁹. Results of both methods were in appreciable agreement with each other and inhibition efficiency was found to depend upon the concentration of inhibitor as well as that of acid. Maximum inhibition

efficiency was shown at highest concentration of Schiff's bases at the highest strength of acid.

Weight loss, potentiodynamic polarisation and electrochemical impedance spectroscopy techniques were adopted for the study of inhibitory action of the synthesized thiosemicarbazones, 4[N-(4'-chlorobenzalidene)amino]antipyrinethiosemicarbazone, 4[N-(benzalidene)amino]antipyrinethiosemicarbazone and 4[N-(4'-methoxybenzalidene) amino]antipyrinethiosemicarbazone towards mild steel corrosion in 4M HCl solution by M. Yadav et. al.⁴⁰. Scanning electron microscopy was used to characterize the surface morphology of the mild steel specimens in the presence and absence of inhibitor. The experimental results showed that the inhibition efficiency increases as the concentration of the inhibitors were increased. The mixed type inhibitory action was indicated by the polarization measurements. The adsorption of studied Schiff bases on mild steel surface obeyed Langmuir adsorption isotherm. Quantum chemical calculations were carried out by semi-empirical AM1 method. A good correlation between the theoretical data and the experimental results was found.

Corrosion inhibitory effects of a novel inhibitor namely 5,5'-[(1Z,1'Z)-(1,4-phenylenebis(methanylylidene))]bis(azanylylidene))bis(1,3,4-thiadiazole-2-thiol) on mild steel in 1.0M HCl was explored by Ahmed A. Al-Amiery et. al.⁴¹ at different temperatures. Results of various electrochemical studies showed that the inhibitory power of the ligand on mild steel increased with concentration and decreased at elevated temperatures. The impedance parameters indicated the adsorption of the inhibitor on the metal surface forming a protective layer is responsible for the inhibitory property.

Scope of the present investigation

The invention of new and improved corrosion inhibitors has now become a challenging task since corrosion is one among the major problems faced by many industrial and research fields. Most of the well known corrosion inhibitors are organic molecule, containing hetero atoms like nitrogen, oxygen, sulphur etc. These inhibitors have electron transfer centres which are capable of forming strong coordinate bond with the metal surface. Several Schiff bases were investigated as corrosion inhibitors for different metals and alloys in acidic media as revealed by the literature survey. The presence of C=N linkage, the electron cloud on aromatic ring, electronegative hetero atoms like nitrogen, oxygen and sulphur in the Schiff base molecule make them excellent corrosion inhibitors. Eventhough the corrosion behaviour of various heterocyclic Schiff bases were studied earlier, only a few of the articles were reported on the corrosion inhibition behaviour of thiophene 2-carbaldehyde Schiff bases.

In the present course of investigation it was proposed to perform the corrosion inhibition study of five novel heterocyclic Schiff bases derived from thiophene-2-carbaldehyde and various amino compounds on mild steel in 1.0M HCl and 0.5M H₂SO₄ solutions, since no works were reported on the anticorrosion behavior of these Schiff bases. The corrosion behavior was analyzed by weight loss measurements, Tafel polarization analysis and electrochemical impedance spectroscopic techniques. The study of corrosion inhibition of these compounds on mild steel is a subject of pronounced technological significance. Also the mechanism of corrosion inhibition is studied by plotting various adsorption isotherms. Thermodynamic parameters such as adsorption equilibrium constant and free energy of adsorptions are also calculated from suitable

adsorption isotherms. The corrosion inhibition efficiencies of the Schiff bases were also compared with that of parent amines.

The effect of temperature on corrosion behaviour of Schiff bases was evaluated to determine the thermodynamic parameters such as activation energy, entropy and enthalpy. In the present study, an attempt was also made to correlate the corrosion inhibition capacity of these molecules with their structural interactions on mild steel surface.