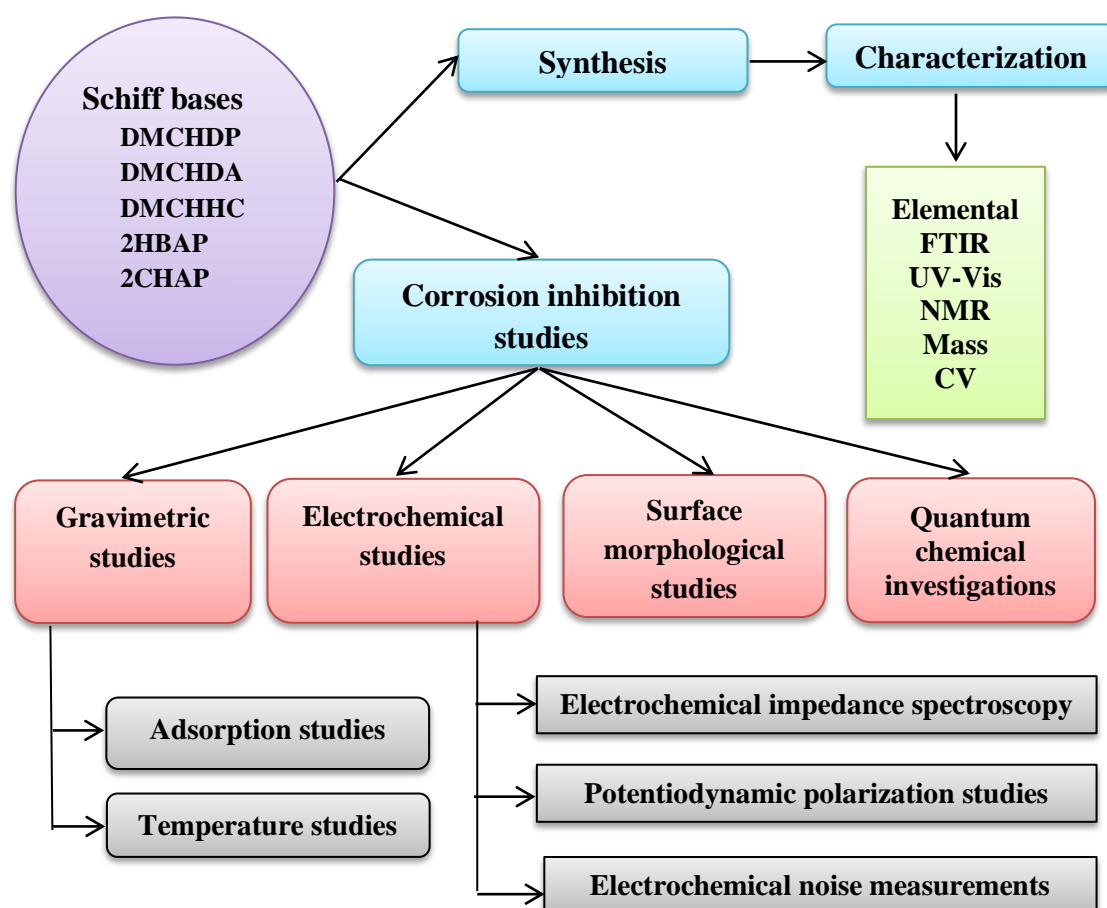


Ragi K “ Structural, corrosion inhibition, chelation, biological and in silico studies of schiff bases.” Thesis. Research and Postgraduate Department of Chemistry, St. Thomas’ college (autonomous), University of Calicut, 2020.

PART I

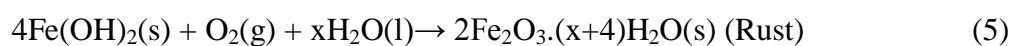
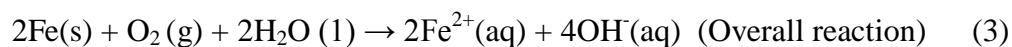
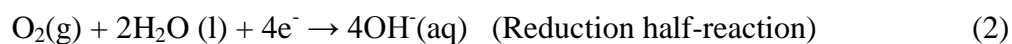
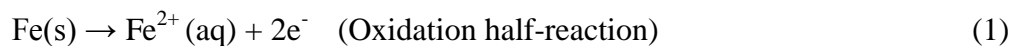
CORROSION INHIBITION STUDIES



CHAPTER 1

INTRODUCTION AND REVIEW

The term corrosion is generally used to describe the interaction of a material with its environment resulting into destruction of the material. It is a natural phenomenon which converts the metal into oxide, sulphide or hydroxide. Rusting of iron is a common example of corrosion. Rate of corrosion enhances in the presence of aggressive acid solutions. Acid solutions are generally used in industries for various purposes such as pickling, oil well acidification, cleaning, descaling etc [1-6]. Hydrochloric acid and sulphuric acid are the commonly used acids in industries. Among various metals mild steels are commonly used for construction purposes owing to its low cost, good weldability and mechanical properties [7-13]. Metallic corrosion is a major threat in industries due to excess use of acids. During the cleaning processes mild steel is attacked severely by the acid solution and gets corroded. As a result quality of the products and efficiency of plants get decreased. Steps involved in the rusting process are mentioned below. First step is the oxidation of iron into Fe^{2+} ion and reduction of oxygen existing in air into hydroxide ion. In the second step the Fe^{2+} and OH^- ions produced will combine to form hydroxide of iron $\text{Fe}(\text{OH})_2$, which on further reaction with oxygen and water present in air to form a reddish-brown solid of hydrated oxide of iron $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, which is generally called as rust. Mechanism of rusting is shown in Fig. 1.1.



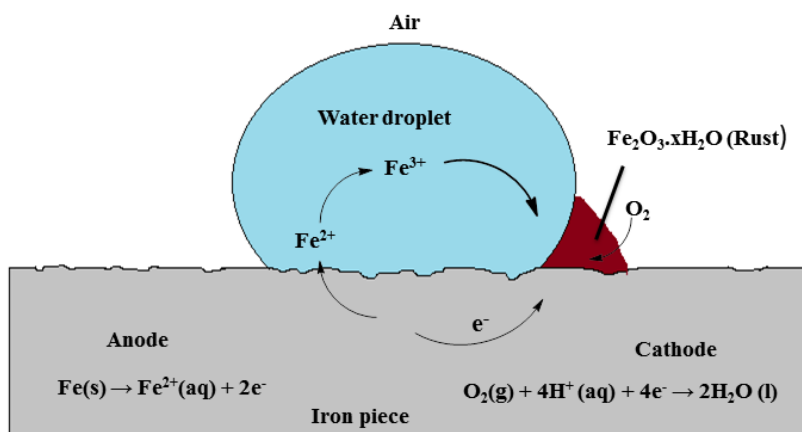


Fig. 1.1 Mechanism of rusting

Economic impact of corrosion

Corrosion is an inevitable process that has serious consequences on the economy of the world. The darkest side of corrosion in a country like India could be better understood if we account the total economic loss occurred in various sectors like infrastructure, utility services, production and manufacturing, defence and nuclear waste which is estimated to be around 1.52 lakh crores. This envisages the fact that corrosion has a deep root in the economic structure of a nation which most often remains unnoticed [14]. It is estimated that an average of 10% of the total metals produced worldwide is deteriorated due to corrosion. In industrialized nations the cost of corrosion is about 3-4% of their GDP. With the exponential economic growths of various sectors extend of corrosion is too increasing to worsen the situation. In countries like Japan and US, corrosion losses are estimated to be about 3% of their respective GDPs. Corrosion has a vital impact on the bottom line of industries, as damage due to corrosion results in increased maintenance cost, lower reliability of equipment, loss of production and poor product quality.

Economic cost of corrosion is classified into two i.e., direct cost and indirect cost. Direct cost is the quantitatively evaluated cost and it includes protection cost, research

and development, investment cost and corrosion inhibition whereas indirect cost is not quantitatively evaluated and it includes contamination of products, decrease in the efficiency of products, loss of revenue due to downtime, loss of products to spill and fire, environmental pollution etc. Estimate of the avoidable costs of corrosion ranges between 10-40%. Direct cost of corrosion is focused in most of the studies even though the impact of indirect cost on corrosion is greater. This is attributed to the difficulties in its estimation. Unfortunately, it is impossible to prevent corrosion, therefore controlling the rate of corrosion by adopting suitable cost effective methods is the most economical solution to its rising challenges [15].

Classification of corrosion

Corrosion is classified according to the nature of degradation of the metal.

Galvanic corrosion: It happens when metals of different substances are placed together in an aggressive electrolyte. A couple is formed between two metals, where one metal act as anode and the other as cathode. More active metal acts as anode and corrodes at an accelerated rate. Affected area is determined by studying the conductivity of the solution.

Uniform corrosion: Also defined as general corrosion which has uniform distribution throughout the surface of the metal. Destruction of protective coating on the metal surface often results in this type of corrosion.

Pitting corrosion: It is a class of localized corrosion results in the formation of small holes in metal. Corrosion of this kind is difficult to find out due to small size and hence more dangerous than uniform corrosion. When a pit is formed it grows into a cavity that takes on different shapes. Generally pits penetrate in the vertical direction from surface to bottom of the metal. It can be created due to non-uniformities in the structure of metal or due to damage of protective oxide film coating.

Crevice corrosion: Corrosion occurring in restricted spaces to which penetration of the working fluid from the environment is reduced. These restricted spaces in general are called crevices. Contact areas between parts, inside cracks and seams, under gaskets, spaces filled with deposits etc are examples of crevices.

Intergranular corrosion (cracking): Also defined as interdendritic or intercrystalline corrosion. It is the cracking preferentially occurring around the grain boundaries under tensile stress. Corrosion of this kind is generally identified using microstructure determination.

Microbial corrosion: This kind of corrosion is usually accelerated by microorganisms. Metal deterioration due to the corrosion process occurring as a result of metabolic activity of microorganisms in cold water systems is called microbiologically induced corrosion (MIC). Anaerobic bacteria will leads to this type of corrosion.

Filiform corrosion: Thread like type of corrosion which develops under protective coating on certain metals usually in humid atmospheres.

Fretting corrosion: Rapid corrosion that occurs at the interface between highly loaded metal surfaces contacted each other when subjected to slight vibrating motions.

High temperature corrosion: Deterioration of a metal due to heating. This can occur when a metal is subjected to a hot atmosphere in the presence of oxygen, sulfur or other compound capable of oxidizing the material.

Factors affecting corrosion

Significant two factors that considerably cause changes in corrosion are nature of metal and environment.

Nature of metal

- Physical state
 - Passive character of metal
-

- Overvoltage
- Purity of metal
- Position in galvanic series
- Relative area of anodic and cathodic parts
- Nature of surface film
- Solubility of corrosion products
- Volatility of corrosion product

Nature of corroding environment

- Humidity of air
- Influence of pH
- Temperature
- Presence of impurities in atmosphere
- Conductance of the corroding medium
- Nature of ions present
- Polarization of electrodes
- Presence of suspended particles in atmosphere
- Flow velocity of process stream

Methods to prevent corrosion

Corrosion is categorized into different classes and they take place under different conditions. Since corrosion is a harmful process it is necessary to take measures to prevent it. Complete prevention of corrosion is difficult to achieve since it is possible only under ideal conditions. Corrosion is the destruction of metal due to its reaction with environment. Therefore the methods adopted to control the rate of corrosion modify the metal or environment.

Modification of metal

Selection of metals/alloys and proper designing: Noble metals and pure metals are corrosion resistant. Since noble metals are not used for general purposes and also such metals are not available in the purest form, their use is limited. Use of alloys which are corrosion resistant is more preferred for general purposes. Designing of equipment and structure is also very important. Simple design and structure is more preferred to control corrosion.

Monitoring the surface of metal: Rate of corrosion will increase when the surface of the metal is rough, crevices or holes is present and because of imperfections during production.

Cathodic protection: In order to control the rate of corrosion the metal surface is taken as cathode in the electrochemical cell. Due to the absence of anodic part on the metal, corrosion does not take place. This can be achieved by two methods such as sacrificial anode protection and impressed current cathodic protection.

Sacrificial anode protection: Electrochemical cell consists of an active metal as anode and metal to be protected as cathode. Hence corrosion will occur only on anode and the metal is protected. Thus the anode used for this purpose is called sacrificial anode. The corroded anodic part is replaced by the new one. Generally aluminium, zinc, magnesium and their alloys are used as sacrificial anode. Low investment cost is required and even economical when protection is required for short period.

Impressed current cathodic protection: System consisting of metal to be protected as cathode and the anode is connected to a DC source. Current is applied in the direction opposite to that of corrosion current to nullify it and to convert the corroding metal from anodic to cathodic nature. Replacement of anode is not required owing to its stable

nature. High investment cost is required and suitable when protection is required for long period.

Modification of environment

Deaeration: Large amount of oxygen dissolved in fresh water will leads to increase in the rate of corrosion. In this method, the dissolved oxygen is removed by agitating mechanically together with rise of temperature.

Coatings: Coating using paint is simple and cost-effective. Paint coatings will prevent the electrochemical charge transfer by acting as a boundary between metal and corrosive medium. Metal coating having high tendency to oxidize over another metal to be protected is called sacrificial coating.

Use of inhibitors: This is the most effective method for reducing the rate of corrosion in acid medium. Inhibitors minimize the corrosion process by raising cathodic or anodic polarization behavior, minimizing diffusion of ions to the metal surface and by raising electrical resistance of metallic surface. Based on the inhibition mechanism, corrosion inhibitors are classified into anodic, cathodic, mixed type and vapor phase inhibitors.

Anodic inhibitors: Also called passivating inhibitors. They protect the metal surface by creating a layer of oxide film on it. They alter the anodic reactions occurring in an electrochemical cell. Passivating inhibitors can be either oxidizing or nonoxidizing. Oxidizing inhibitor passivates metal in the absence of oxygen. Nitrite, chromate, nitrate etc are some examples. Non oxidizing inhibitor passivates metal in the presence of oxygen. Tungstate, molybdate, phosphate etc are some examples. The concentration of the inhibitor must be high in solution. Insufficient amount of inhibitor will leads to localized corrosion since the surface is not completely covered by the inhibitor.

Cathodic inhibitors: Inhibitors that minimizes the cathodic reaction and limit migration of ions to cathodic area. They inhibit by acting as cathodic poisons, cathodic

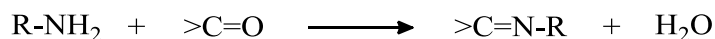
precipitates and oxygen scavengers. Sulphites, bicarbonates etc are some examples. Low concentration of inhibitor is required and hence more secure than anodic inhibitors.

Organic inhibitors: Organic inhibitors are used on a wide scale in industries. They are less toxic, had the ability to exist together with the protected metal, highly soluble and effective at different range of temperatures. They can act as anodic, cathodic or mixed inhibitor by adsorbing on the metal surface forming a film. Amines, quaternary ammonium salts, pyridine derivatives, amino acids, Schiff base, indazole, derivatives of imidazole, triazole, oxazol, thiadiazole, thiourea, thiazole and phtalimides, plant extracts and sulfonates are some examples of organic inhibitors. Schiff bases are well-known example for organic inhibitors. They are prepared by condensing an amino compound with aldehyde or ketone and having a general formula $R_2C=NR$. Literature survey revealed that Schiff bases are good corrosion inhibitors on comparing with the parent compounds from which they are synthesized. This is due to the participation of $-CH=N-$ group present in Schiff base molecules [16-18]. They can adsorb on the surface of the metal by means of both physical and chemical interaction [19-21]. Adsorption process is supported by structure of the inhibitor molecule, nature of metal surface and corrosive environment. The lone pair of electrons present on hetero atoms such as N, O and S, unsaturated π bonds, conjugated aromatic rings and planarity of the molecules are the most important characteristics that control adsorption of inhibitor molecules on the metal surface [22-25].

Schiff bases

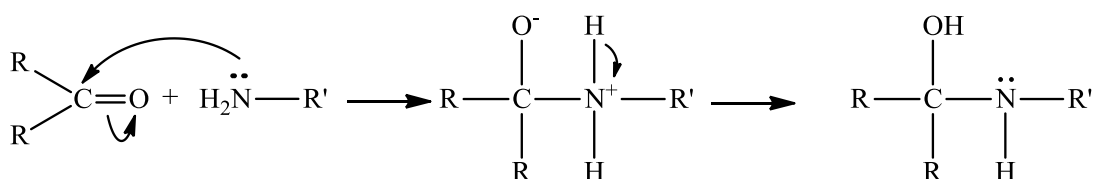
German chemist Hugo Schiff discovered Schiff base in 1864 [26]. Schiff bases are generally prepared by the condensation of carbonyl compounds (aldehyde/ketones) with aromatic or aliphatic primary amines. It is regarded as a nitrogen analogue of an

aldehyde or ketone where imine group substitutes C=O group and also known as imine or azomethine.

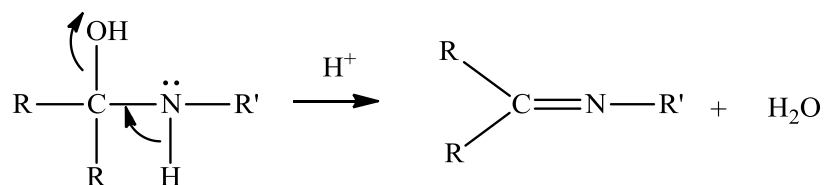


In the case of aldehydes the C=O group has less steric hindrance than ketone, hence it can form Schiff base more easily. Generally Schiff bases containing alkyl substituents can be easily polymerize and are unstable whereas that containing aryl substituents are stable due to effective conjugation. Schiff base formation is usually reversible and generally occurs upon heating or when acid or base is present. Generally Schiff base is formed through two steps. First step is the nucleophilic addition of primary amine to carbonyl group which leads to the formation of an unstable product carbinolamine. In the second step (rate determining step) acid catalyzed dehydration of the alcohol (carbinolamine) will take place. So the reaction involves an addition followed by an elimination reaction.

Step1: Carbinolamine formation



Step2: Acid catalyzed dehydration



Acid concentration had a great role in the synthesis of Schiff bases. Very high concentration of acid will lead to protonation of amines and hence loses its nucleophilicity. Also in acidic environment, the Schiff bases may sometimes hydrolyzed

back to its parent carbonyl compound and amine. Therefore mild acidic pH is preferable for Schiff base synthesis.

Denticity can vary from bidentate to polydentate in the case of Schiff base ligands. Donor atom present in it offers special capability to bind with metals. They can able to bind with various metal atoms and to stabilize metal atoms in different oxidation states. Incorporation of metals in the lattice of donor atoms will change the morphological, pharmacological and physiological properties of the Schiff base compounds. Their chelating ability with both transition and non-transition metal ions are very high. Sensitivity, selectivity, presence of azomethine group and synthetic flexibility of the Schiff base ligands makes them an important class of ligands.

Importance of Schiff bases

Schiff base ligands have extensive applications in various fields such as analytical, inorganic, organic and biological fields [27-30]. The lone pair of electrons in the sp^2 hybrid orbital of N atom in ($-C=NH-$) linkage present in Schiff bases enhances their biological and chemical importance [31-32]. They have excellent pharmacological activities and are widely used in pharmaceutical industry. Preparation of Schiff bases is comparatively easy, possess attractive features and have structural similarity with naturally occurring biological substances [33-34]. Large number of Schiff bases prepared from aromatic aldehydes and aromatic amines are used as fluorimetric analytical reagents [35]. Chiral Schiff bases are found to be a good catalyst in enantioselective Henry (nitro aldol) reaction [36]. The antibacterial, antitumor, antifungal, anti-inflammatory, catalytic, anti-HIV, anticonvulsant and antioxidant activities are reported in many literatures [37-44]. In many enzymatic reactions Schiff bases are found to be a prominent intermediate. Biochemical process involving such enzymatic reactions is condensation of primary amine of a lysine residue present in an enzyme with carbonyl

group present in the substrate forming Schiff base ligand [45]. Schiff bases have particularly significant applications in four types of reaction such as 1) hetero Diels-Alder reaction to furnish six membered nitrogen containing heterocyclic compounds 2) addition of organometallic reagents or hydride to C=N bond 3) skeletons for the building-up scaffolds, as the very famous salen scaffold, to be used as “privileged ligand” for the formation of the corresponding chiral salen metal complexes 4) Staudinger reaction with ketene to furnish biologically important β -lactam ring [46].

Malaria is a severe morbidity of humans and other animals. It is caused by protozoa of the genus *Plasmodium*. It is initiated by a bite from an infected female *Anopheles* mosquito, which introduces the *Plasmodium* through saliva into the circulatory system. In the blood, the protists travel to the liver to mature and reproduce. Typical symptoms of malaria include fever and headache, which in severe cases, can progress to coma and eventually death [47]. The imino-group of Schiff bases has shown valuable function to confer antimalarial activity. Schiff bases are also intermediate in bioprocesses such as transamination reaction [48]. The -C=N- present in Schiff bases can be easily reduced by complex metal hydrides and is a method for the formation of amino compounds. Similarly hydrogen cyanide addition to Schiff bases takes place easily and provides a feasible path for the formation of α -amino nitriles (Strecker synthesis). [1+2] Cycloaddition reactions of carbenoids and carbenes to Schiff bases are also reported in literature [49]. Another important characteristic of Schiff bases is their good chelating ability [50-53]. Azomethine group present in it has the potential to coordinate with almost all metals by coordinating through N atom. In order to reduce or prevent rate of corrosion of metallic substances in acidic environment corrosion inhibitors are widely used in industries. Azomethine linkage present in Schiff bases is responsible for the

complex formation with metal ion and thereby inhibits the corrosion. They create a barrier to moisture and oxygen by adsorbing on the surface of the metal [54].

Schiff bases as corrosion inhibitors in acid media- A review

Generally organic compounds having reactive centers such as hetero atoms, lone pair of electrons, aromatic rings, and delocalized π electrons are proved to be effective inhibitors of metallic corrosion in various environments. Schiff base is an organic compound satisfying all these features and found to be a potential corrosion inhibitor. Role of Schiff bases as an excellent corrosion inhibitor in various metals like mild steel, zinc, copper and aluminium in aggressive acid media like sulphuric acid, hydrochloric acid etc were already reported by researchers.

S. John et al. investigated the corrosion inhibition capacity of the compound 4-(N,N-dimethylaminobenzilidene)-3-mercapto-6-methyl-1,2,4-triazin(4H)-5-one (DAMMT) on mild steel in 1 M HCl using gravimetric method, electrochemical methods such as electrochemical impedance spectroscopy, potentiodynamic polarization (Tafel and linear polarization) and quantum chemical calculation [55]. Langmuir isotherm was found to be the best fit isotherm. It was found that DAMMT is an excellent inhibitor towards mild steel and also acts as a mixed type inhibitor. From the results it is clear that inhibition efficiency is found to increase with concentration and decreases with higher exposure time at 300 K. Structure of DAMMT is shown in Fig. 1.2.

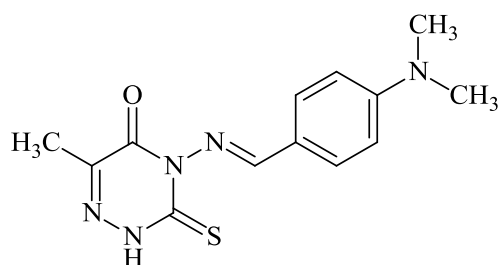


Fig. 1.2 Structure of DAMMT

The inhibiting nature of four Schiff bases, 2-((1Z)-1-aza-2-(2-pyridyl)vinyl)pyrimidine, 2-((1E)-2-aza-2-(1,3-thiazol-2-yl)vinyl)thiophene, 2-((1E)-2-aza-2-pyrimidine-2-ylvinyl)thiophene and 2-((1Z)-1-aza-2-(2-thienyl)vinyl)benzothiazole on the corrosion of carbon steel in 0.1 M HCl was investigated by A. Yurt et al. using electrochemical impedance studies and potentiodynamic polarization studies [56]. Polarization data revealed that all the four Schiff bases acted as anodic inhibitors. Inhibition efficiency was found to vary with the nature of substituent group present in the molecule. Temkin adsorption isotherm was the most-fit isotherm for all the Schiff bases. Study of impact of temperature on the corrosion inhibition efficiency showed that efficiency decreased with rise in temperature.

W. Li and co-workers studied the influence of two triazole derivatives 2,5-dichloro-acetophenone-O-1'-(1',3',4'-triazolyl)-methaneoxime (5-DTM) and 3,4-dichloro-acetophenone-O-1'-(1',3',4'-triazolyl)-methaneoxime (4-DTM) on corrosion of mild steel in 1 M HCl using weight loss, impedance and SEM studies [57]. Both triazole derivatives are found to exhibit good inhibition potency and acted as mixed type inhibitors. Excellent inhibition capacity was shown by these compounds at 1mM concentration according to weight loss studies. Results obtained from weight loss studies are in good agreement with electrochemical studies. Adsorption of triazole derivatives on MS in 1 M HCl was found to obey Langmuir adsorption isotherm.

K. M. Govindaraju et al. synthesized three Schiff bases of 4-amino-antipyrine and evaluated the influence of these Schiff bases (4-[(4-methoxy benzylidene)-amino]-antipyrine (AAAP), 4-[(benzylidene)-amino]-antipyrine (BAAP) and 4-[(4-hydroxy benzylidene)-amino]-antipyrine (SAAP)) and 4-amino-antipyrine (AAP) on corrosion of mild steel in acid media [58]. Techniques used for this purpose were weight loss, impedance, potentiodynamic polarization and FT-IR. From the studies, it is clear that the

Schiff bases are exhibiting very good inhibition capacity when compared to 4-amino-antipyrine. The order of efficiency is AAAP>SAAP>BAAP>AAP. All the Schiff bases acted as mixed type inhibitor according to polarization studies. Maximum inhibition potency of 90.83% was exhibited by AAAP at 0.8 mM concentration.

N. Kuriakose and co-workers synthesized thiophene-2-carbaldehyde tryptophan and investigated its corrosion inhibition capacity using weight loss and electrochemical studies on mild steel (MS) in 1 M HCl solution [59]. Results proved that the ligand is a very good inhibitor and efficiency increased with concentration. Freundlich isotherm was obeyed and evaluated thermodynamic parameters. Also it acted as mixed type inhibitor.

M. G. Hosseini et al. conducted electrochemical studies such as electrochemical impedance spectroscopy (EIS) and Tafel polarization to evaluate the inhibition of mild steel corrosion in 0.5 M H₂SO₄ solution by three Schiff bases N,N'-ethylen-bis(salicylideneimine) [S1], N,N'-isopropyl-bis(salicylideneimine) [S2] and N-acetyl acetone imine, N'-(2-hydroxybenzophenone imine)ortho-phenylen [S3] [60]. Maximum inhibition potency of ~97-98% was shown by these Schiff bases at 300 ppm concentration. S2 was more effective than the other two Schiff bases. The nature of adsorption is physical and obeyed Langmuir adsorption isotherm.

Theoretical and corrosion inhibition studies were done by I. Ahamad et al. to examine whether there is any relation between the results obtained from both studies [61]. The Schiff base 2-[2-(2-(3-phenylallylidene)hydrazine carbonothioyl)hydrazine carbonyl]benzoic acid acted as an excellent corrosion inhibitor for MS in 1 M hydrochloric acid medium. Maximum efficiency of about 99.5% is shown by the inhibitor at 1.369×10^{-6} M concentration. Protective film formation of the inhibitor on metal surface was confirmed by FTIR technique. Schiff base acted as a mixed type

inhibitor and the mechanism of adsorption is chemisorption. Parameters obtained from theoretical studies are in good agreement with that of corrosion studies.

Gravimetric, EIS, polarization and theoretical studies of three bis-Schiff bases (2-methoxybenzylidene)hydrazono)indolin-2-one (HZ-1), (2-hydroxybenzylidene)hydrazono)indolin-2-one (HZ-2) and (4-nitrobenzylidene)hydrazono)indolin-2-one (HZ-3)) of isatin was carried out by K. R. Ansari et al. to study the capability of reducing the corrosion of mild steel in 1.0 M HCl medium [62]. Order of inhibition efficiency was $\text{HZ-1} > \text{HZ-2} > \text{HZ-3}$. All the three inhibitors are mixed type and obeyed Langmuir adsorption isotherm. Surface morphological studies (SEM and EDX) were employed to confirm the protective film formation on metal surface. Quantum chemical and corrosion inhibition studies were in good correlation.

K. S. Shaju et al. synthesized the Schiff base anthracene-9(10H)-one-3-aminopropanoic acid (A9O3AP) and studied the effect of KI on its corrosion inhibition efficiency on mild steel in 0.5 M H_2SO_4 by means of weight loss, electrochemical impedance and potentiodynamic polarization studies [63]. Inhibition efficiency was found to increase with concentration and synergistic effect of KI was also observed. That is corrosion inhibition efficiency enhanced when KI is added. Freundlich and Langmuir isotherms were obeyed by inhibitor and inhibitor + KI on the metal surface. Thermodynamic parameters were also evaluated and it acted as mixed type inhibitor.

M. A. Quraishi et al. investigated the behaviour of five substituted dianils namely 1,4-di-dimethylaminobenzylideneaminophenylene (DDAP), 1,4-divanilledeneamino phenylene (DVAP), 1,4-disalicyledeneaminophenylene (DSAP), 1,4-dibenzylidene aminophenylene (DBAP) and 1,4-dicinnamylideneaminophenylene (DCAP) as inhibitor for mild steel corrosion in 1 N HCl and 1 N H_2SO_4 [64]. Among these compounds DCAP is the best inhibitor in both acid media. Variation of efficiency with concentration, nature

of the compound, immersion time and temperature were also evaluated. All inhibitors acted as mixed type inhibitors and obeyed Temkin adsorption isotherm.

Corrosion inhibition potency of three newly synthesized Schiff bases derived from aromatic aldehydes and L-lysine in 1 M HCl was evaluated using electrochemical, gravimetric, SEM, EDX and AFM methods by N. K. Gupta et al [65]. Efficiency was found to be increased with concentration and maximum inhibition efficiency of 2-amino-6-((4-dimethylamino)benzylideneamino)hexanoic acid at a concentration of 400 mgL^{-1} is 95.6%. Polarization data showed that all Schiff bases are cathodic inhibitors and obeyed Langmuir isotherm in hydrochloric acid medium.

Schiff bases of salicylaldehyde and cyclic ketones as corrosion inhibitors in acid media- A review

A. M. Abdel-Gaber and co-workers investigated the corrosion inhibition capacity of N,N' -bis(salicylaldehyde)-1,3-diaminopropane (Salpr) and its Co complex on steel in 1 M H_2SO_4 by EIS and polarization studies [66]. Stability of Co complex in acid media was examined by using spectrophotometry measurements. Adsorption behaviour was clarified using different isotherms. Results showed that Co complex has good corrosion inhibition effect than corresponding ligand. Structure of Salpr is shown in Fig. 1.3.

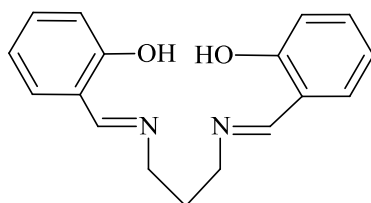


Fig. 1.3 Structure of Salpr

Corrosion inhibition of mild steel in 1 M HCl by Schiff bases derived from 4-amino antipyrine and salicylaldehyde/furfuraldehyde/anisaldehyde was evaluated using gravimetric and electrochemical studies by Balaji. M et al [67]. Results obtained from both studies were in good agreement and they inhibit corrosion by adsorbing on the

metal surface. Charge transfer resistance increased and double layer capacitance decreased with concentration. Polarization studies revealed that they are mixed type inhibitors.

S. P. Fakrudeena et al. synthesized the ligands N,N'-bis (3-methoxy salicylidene)-1,4-diaminophenylene (MSDP) and N,N'-bis(salicylidene)-1,4-diaminophenylene (SDP) [68]. Weight loss and SEM technique were used to evaluate the corrosion inhibition of SDP and MSDP on AA6061 and AA6063 alloy in 1 M HCl medium. Inhibition efficiency was found to increase with rise in concentration and alter with immersion time and solution temperature. Both Schiff bases obeyed Freundlich adsorption isotherm and MSDP was found to be an effective inhibitor than SDP.

Three Schiff bases have been derived from salicylaldehyde/p-chloroaniline, salicylaldehyde/N,N'-ethylenediamine and cinnamaldehyde/N,N'-ethylenediamine by P. Karuppasamy and co-workers [69]. The corrosion inhibition of these Schiff bases on mild steel in hydrochloric acid medium were evaluated using weight loss, impedance, potentiodynamic polarization, IR and UV-visible studies. Langmuir isotherm was obeyed by all the Schiff bases and they acted as mixed type inhibitors.

A. Barbosa da Silva et al. reported that the anti-corrosive behaviour of the reduced form (N,N'- bis(2-hydroxybenzyl)-1,2-ethylenediamine) is greater compared to N,N'-bis(salicylidene)-1,2-ethylenediamine (Salen) and mixture of parent compounds salicylaldehyde and ethylene diamine on carbon steel in 1 M HCl medium [70]. Corrosion monitoring was done by EIS, polarization study, spectrophotometry and corrosion potential measurements. Results showed similar inhibition efficiency for Salen and mixture of its corresponding parent compounds. This is attributed to the hydrolysis of Salen in acid medium. Structure of Salen is shown in Fig. 1.4.

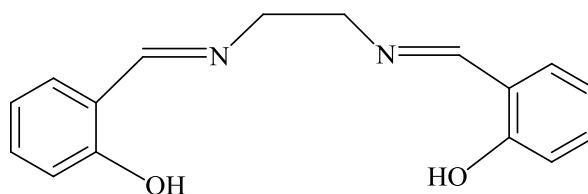


Fig. 1.4 Structure of Salen

R. Menaka et al. studied inhibition efficacy of Schiff base derived from chitosan and salicylaldehyde on mild steel in 1 M HCl medium adopting weight loss and electrochemical studies [71]. Characterization of the Schiff base was done by FTIR, Ultraviolet spectroscopy, elemental and SEM analysis. Thermal stability of the compound was also determined. Temkin isotherm is obeyed by the chitosan Schiff base and the adsorption is chemical in nature. SEM analysis confirmed the protective layer formation of the Schiff base on mild steel surface.

A novel Schiff base 2-((5-mercapto-1,3,4-thiadiazol-2-ylimino)methyl)phenol (MTMP) has been synthesized by R. Solmaz et al. and its inhibiting action on the corrosion of mild steel in 0.5 M HCl solution was investigated by weight loss and electrochemical studies [72]. Schiff base acted as a mixed inhibitor and obeyed Langmuir adsorption isotherm. Inhibition efficiency was concentration dependent and reached a maximum value of 97% at 1 mM. Structure of MTMP is shown in Fig. 1.5.

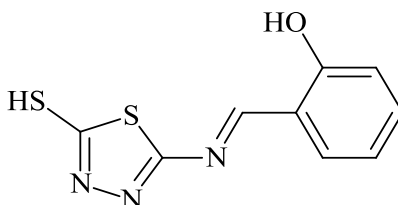


Fig. 1.5 Structure of MTMP

A. S. Fouda et al. synthesized N-3-hydroxyl-2-naphthoyl hydrazone derivatives of 2-acetophenone, α -tetralone, benzaldehyde and cyclohexanone and investigated corrosion inhibition efficiency of these derivatives on carbon steel in 0.5 M H₂SO₄ [73]. Corrosion monitoring techniques used were weight loss method and polarization

measurements. Study showed that these derivatives were mixed type inhibitors and obeyed Frumkin adsorption isotherm. Synergistic effect of KBr, KI and KSCN on enhancing the corrosion inhibition efficiency of the compounds was also studied.

Schiff bases of 2-aminophenol as corrosion inhibitors in acid media- A review

K. Veni and co-workers synthesized Schiff base derived from o-aminophenol and p-chlorobenzaldehyde and its transition metal complexes using grinding method [74]. Characterization was done using IR, UV, NMR, Mass and ESR spectroscopic techniques and molar conductivity studies. Corrosion inhibition study of the ligand and its complexes on mild steel surface were conducted using weight loss measurement in 0.1 M HNO₃. Promising inhibition efficiency was observed for the compounds.

Corrosion inhibition nature of the Schiff bases obtained by the condensation of 2-aminophenol with acrolein, 2-aminophenol with cinnamaldehyde and phenylene diamine with cinnamaldehyde on carbon steel in 0.5 N HCl were investigated using weight loss and electrochemical studies by M. Q. Mohammed [75]. IR, UV, ¹H NMR and CHN analysis were carried out for the characterization. Results obtained from both corrosion monitoring techniques are in good agreement and exhibiting good inhibition efficiency.

Y. B. Zemedet et al. studied corrosion inhibition efficiency of the Schiff base ligand (2E)-2-((5-((E)-(2-hydroxyphenylimino)methyl)thiophene-2-yl)methylene amino) phenol and its Co(II), Ni(II), Cu(II) and Zn(II) complexes using weight loss measurement in 0.1 M HCl for MS specimen [76]. Metal complexes are found to exhibit high inhibition efficiency than the ligands. The order of efficiency was [CoL(H₂O)₂] > [NiL(H₂O)₂] > [ZnL] > [CuL] > L, where L= ligand. Higher efficiency of complexes may be due to planarity and large size of the molecule. They inhibit the corrosion by adsorbing on the metal surface.

Gravimetric and electrochemical studies were adopted to evaluate inhibition efficiency of the ligands 2-(5-chloro-2-hydroxybenzylideneamino)phenol, 2-(2-hydroxybenzylideneamino)phenol and 2-(2-hydroxy-5-nitrobenzylideneamino)phenol against MS corrosion in 1 M HCl by S. K. Saha et al [77]. Surface morphological studies were carried out in the presence and absence of inhibitor to confirm the adsorption of ligand on metal. Corrosion inhibition efficiency is found to increase with increase in concentration of inhibitor. Polarization study revealed that they are mixed type inhibitors. All the ligands obeyed Langmuir adsorption isotherm on mild steel surface. Quantum chemical calculations were also carried out to determine the relation between structure of the molecule and the inhibition efficiency. There exist good interdependence between the experimental results and theoretical data.

Schiff bases of aniline as corrosion inhibitors in acid media- A review

P. Silku and co-workers synthesized and characterized acryloyl derivatives of Schiff base derived by the reaction of *p*-hydroxybenzaldehyde with aniline, *p*-nitroaniline, *p*-aminobenzoic acid, *p*-chloroaniline and *p*-methylaniline [78]. Spectroscopic tools like IR, UV-Vis, NMR and mass technique were adopted for characterization. UV-Vis study was done in three different solvents depending on the solubility of the ligand and derivatives. Corrosion inhibition efficiency of all the compounds on steel surface were investigated in 0.1 M NaOH, 0.1 M NaCl and 0.10 M H₂SO₄ medium with the aid of Tafel and cyclic voltammetric studies.

The corrosion inhibition efficiency of the Schiff bases N-(furfurilidene)-4-methyl aniline, N-(cinnamalidene)-4-methoxyaniline, N-(furfurilidene)-4-methoxyaniline, N-(salicylidene)-4-methoxyaniline and N-(cinnamalidene)-2-methylaniline on mild steel in H₂SO₄ was monitored using weight loss and thermometric methods by Upadhyay et al [79]. Results obtained from both methods are in good agreement and inhibition

efficiency depends on the concentration of inhibitor and acid medium. At highest concentration of Schiff base at the highest strength of acid, the inhibition efficiency is found to be maximum.

D. Daoud et al. investigated corrosion inhibition efficiency of the Schiff base synthesized from 4-[(4-aminophenyl)methyl]aniline and thiophene-3-carbaldehyde on mild steel X52 in 1 M HCl and 1 M H₂SO₄ with the aid of corrosion monitoring techniques such as weight loss, electrochemical impedance spectroscopy and potentiodynamic polarization studies [80]. Results showed that the synthesized Schiff base was an excellent corrosion inhibitor and the inhibition efficiency rise with inhibitor concentration. Langmuir adsorption isotherm was obeyed. Relation between inhibition efficiency of the studied Schiff base and quantum chemical calculation was also discussed using density functional theory (DFT) method.

M. Farsak and co-workers synthesized the Schiff base (E)-N-((E)-3-phenyl allylidene)-2-(phenylthio)aniline (2-PTA) and studied its corrosion inhibition efficiency on low carbon steel (LCS) in HCl medium for a wide range of temperature using electrochemical methods such as electrochemical impedance spectroscopy and potentiodynamic polarization studies [81]. The inhibitor 2-PTA is found to possess 99.8% corrosion inhibition efficiency after 120 h immersion time in 1 M HCl medium containing 2.5 mM inhibitor molecule. Results showed that the inhibitor 2-PTA was adsorbed on LCS to a larger extent at all temperatures. Tafel technique revealed that the inhibitor is cathodic controlled mixed type inhibitor at all temperature. Isotherm obeyed by 2-PTA on LCS is Langmuir adsorption isotherm. Larger value of K_{ads} also supports the higher adsorption ability of the inhibitor on metal surface. Structure of 2-PTA is shown in Fig. 1.6

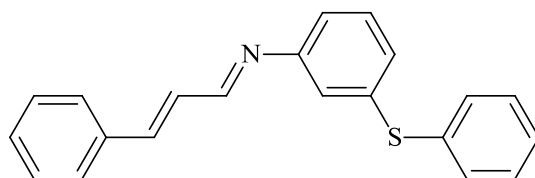


Fig. 1.6 Structure of 2-PTA

The effect of Schiff base (Z)-4-chloro-N-((2-chloroquinolin-3-yl) methylene) aniline (4-CCMA) on the corrosion of mild steel (MS) in 1 N HCl was examined using weight loss, impedance, potentiodynamic polarization and SEM analysis by Bhupendra M. Mistry et al [82]. Inhibition efficiency was found to rise with inhibitor concentration and exhibiting maximum efficiency of 99.04 % at 25 ppm of 4-CCMA. The inhibitor 4-CCMA serves as mixed type inhibitor according to polarization studies. Charge transfer resistance was found to increase with concentration of 4-CCMA in accordance with impedance study. Adsorption studies revealed that Langmuir adsorption isotherm was followed by the inhibitor. Impact of temperature on the corrosion inhibition of mild steel in 1 N HCl was also investigated in the range of temperature from 298-318 K. Structure of 4-CCMA is shown in Fig. 1.7.

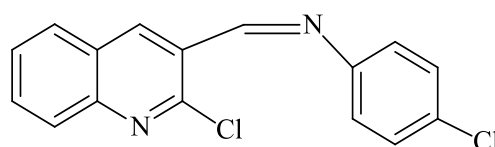


Fig. 1.7 Structure of 4-CCMA

Schiff bases of semicarbazide and thiosemicarbazide as corrosion inhibitors in acid media- A review

V. P. Raphael et al. carried out weight loss, EIS and polarization studies to determine the corrosion inhibition property of 3-acetylpyridinesemicarbazone (3APSC) on carbon steel in 1 M HCl [83]. From the results it is clear that 3APSC has significant inhibition even at low concentration. Adsorption obeyed Langmuir isotherm and it acted as mixed type inhibitor. Thermodynamic parameters such as activation energy, enthalpy

of corrosion and entropy of correction were also calculated. SEM analysis was also carried out to study the surface nature of the metal. Structure of 3APSC is shown in Fig. 1.8.

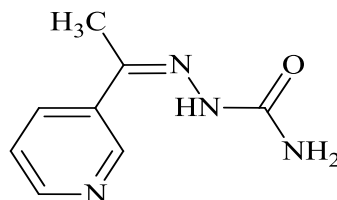


Fig. 1.8 Structure of 3APSC

Corrosion inhibition effect of mild steel in 1 M HCl by vanillinthiosemicarbazone and its ethyl and methyl derivatives were analysed using weight loss, impedance and potentiodynamic polarization studies by T. S. Franklin Rajesh and co-workers [84]. Inhibitors were found to exhibit good corrosion inhibition property even at 10^{-3} M concentration. Parent compounds were also subjected to corrosion inhibition studies. Result obtained from all the three methods are in good correlation. The three inhibitors are of mixed type and obeyed Langmuir adsorption isotherm.

Inhibiting nature of two semicarbazones (2-indolecarboxaldehyde/2-pyridine carboxaldehyde and semicarbazide hydrochloride) and four thiosemicarbazones (4-ethoxybenzaldehyde/ 4-hydroxybenzaldehyde/ 4-hydroxy-3-methoxybenzaldehyde/ 2-pyridinecarboxaldehyde and thiosemicarbazide) on the corrosion of carbon steel in 0.1 M HCl was investigated by C. M. Goulart et al. using electrochemical impedance spectroscopy, potentiodynamic polarization and molecular modelling at different inhibitor concentration [85]. Charge transfer resistance was found to increase with inhibitor concentration in impedance plots. Polarization studies revealed that the inhibitors acted as mixed type inhibitors.

V. P. Raphael and co-workers synthesized and characterized two heterocyclic semicarbazones (E)-2-((5-(4-nitrophenyl)-furan-2-yl)methylene)hydrazinecarboxamide

(NPFASC) and (E)-4-(5-((2-carbamoylhydrazano)methyl)furan-2-yl)benzoic acid (CPFASC) [86]. Corrosion inhibition capacity of the compounds on carbon steel surface in 1 M HCl medium by weight loss, EIS and polarizations studies were also investigated. Results showed that despite of non-planar structure of NPFASC, it is a more effective inhibitor than CPFASC. This is due to the reduction of NO_2 group present in NPFASC into NH_2 group when come close to metal surface in acid medium. Geometry of the molecule NPFASC will change in favour of corrosion inhibition as a result of this conversion. El-Awady and Freundlich isotherms were obeyed by NPFASC and CPFASC respectively. Surface morphological studies were also carried out using IR, AFM and SEM. Structure of CPFASC and NPFASC is shown in Fig. 1.9.

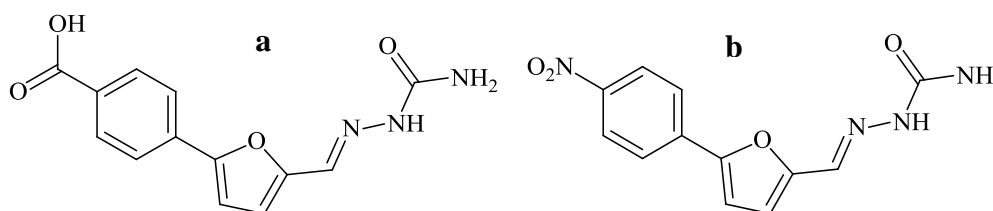


Fig. 1.9 Structure of a) CPFASC b) NPFASC

Three thiosemicarbazones and two semicarbazones such as 2-acetylpyridine-(4-methyl)thiosemicarbazone (2AP4MTSC), 2-acetylpyridinethiosemicarbazone (2APTSC), 2-acetylpyridine-(4-phenyl)thiosemicarbazone (2AP4PTSC), 2-acetylpyridine semicarbazone (2APSC) and 2-acetylpyridine-(4-phenyl)semicarbazone (2AP4PSC) were synthesized and their corrosion inhibition property was monitored using hydrogen evolution via the gasometric assembly at 30°C and 40°C in 5 M H_2SO_4 by P. C. Okafor and co-workers [87]. It is observed that thiosemicarbazones enhances the corrosion rate at low concentration and reduced the corrosion rate at higher concentrations. Semicarbazones enhanced the corrosion rate at all concentrations. Inhibition efficiency follows the order $2\text{AP}4\text{PTSC} > 2\text{AP}4\text{MTSC} > 2\text{APTSC} > 2\text{AP}4\text{PSC} > 2\text{APSC}$.

Dr. L. Ravikumar et al. evaluated corrosion inhibition efficiency of the Schiff bases *r*-2,*c*-6-diphenyl-*t*-3-methyl piperidine-4-one [S₁], *r*-2,*c*-6-diphenyl-*t*-3-methyl-*N*-methyl piperidine-4-one semicarbazone [S₂] and *r*-2,*c*-6-diphenyl-*t*-3-methyl piperidine-4-one semicarbazone [S₃] on mild steel in 1 M H₂SO₄ by means of weight loss, impedance, potentiodynamic polarization and scanning electron microscopic technique [88]. Inhibition efficiency was found to increase with concentration and at a concentration of about 7 mM, inhibition efficiency reaches a maximum value of 93-94% in all cases. The semicarbazone S₂ was more efficient than other two semicarbazones. The isotherm obeyed was Langmuir adsorption isotherm.

Scope and aims of present investigations

Corrosion is a serious issue that challenges scientists and researchers. The corrosion inhibition efficiency of a wide range of organic molecules has been screened by various researchers. Among them, Schiff bases are proven to be an effective corrosion inhibitor by adsorbing on the surface of the metal. The active part present in Schiff base molecules which is responsible for corrosion prevention is azomethine linkage. In addition to this, presence of lone pair of electrons on hetero atoms such as N, O and S, unsaturated π bonds, aromatic rings and planarity of the molecule are the most important characteristics that enhance adsorption of inhibitor molecules on the metal surface. Despite the fact that various Schiff base molecules have been screened for their corrosion inhibition potency, search for new Schiff base molecules for preventing corrosion has key importance in industrial and research fields.

In the present course of investigation it was proposed to carry out synthesis, characterization and checking corrosion inhibition efficiency of five Schiff base ligands derived from 5,5-dimethylcyclohexanone, salicylaldehyde and cyclohexanone with various amino compounds on mild steel in 1.0 M HCl and 0.5 M H₂SO₄ medium by

weight loss studies and electrochemical studies such as electrochemical impedance spectroscopy, potentiodynamic polarization studies and electrochemical noise measurements. Corrosion inhibition studies of the parent compounds also to be investigated to check the argument that the active part present in Schiff base molecules which is responsible for corrosion prevention is azomethine linkage. Corrosion inhibition mechanism is to be explored with the aid of adsorption isotherms. Thermodynamic parameters such as free energy of adsorption and adsorption equilibrium constant were also proposed to evaluate from adsorption isotherms.

Temperature dependent gravimetric corrosion investigations were employed to determine thermodynamic parameters such as activation energy (E_a), enthalpy of activation (ΔH^*), entropy of activation (ΔS^*) and Arrhenius parameter (A). Scanning electron microscopic analysis can be utilized to understand surface morphology of the mild steel specimens. Quantum chemical investigations will also perform to correlate the relationship between corrosion inhibition efficiency and electronic properties of the molecule.