

Review on Mechanistic Action of Inhibitors on Steel Corrosion in Acidic Media

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Abstract

Use of inhibitor is proven as an efficient and widely accepted corrosion prevention method. Corrosion control of steel is an important activity in technical, economic, environmental and safety terms. This article enumerates several types of inhibitors used to combat corrosion in acidic medium. In this paper, literature on corrosion inhibitors has been reviewed and discussions are made on properties and efficiency of inhibitors. (The prominent features of our work on the mechanism of corrosion inhibitors have been highlighted and in a few cases have tried to predict its mechanism).

Keywords: Inhibitor, Mechanism, Acid corrosion, Quantum studies.

Introduction

Corrosion is a process in which loss of essential properties of material occurs as a result of its interaction with surroundings. In spite of remarkable advancement in the field of corrosion science and technology, the phenomenon of corrosion remains a major obstacle for industries all over the world. Though corrosion can be controlled by adapting suitable methods and highly corrosion resistant materials, it accounts for additional expenditure. So, industries would like to prefer the use of cheap metallic materials along with a suitable protection method, and the method selected for this purpose is based on its cost and performance in the field. Steel is one such material, which has been used in desalination plants, construction materials, pharmaceutical industry, thermal power plants, plating industries, oil refineries, automobiles, etc. Steel, in addition, has good mechanical and metallurgical properties which are very much essential for its fabrication for different applications. The surface preparation of steel materials is often done in industries to obtain a clear and highly active surface for further processing. For this operation, some strong acid solutions, such as H₂SO₄ or HCl are used as pickling liquors for surface cleaning of iron

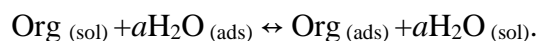
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and steel materials. The highly corrosive nature of these acids affects steel surface. Hence, steel surface needs protection to achieve its minimum loss. Use of corrosion inhibition is one such best available methods to minimize the loss of steel [1-3].

For this purpose, the organic compounds containing N, P, S, and O in their molecular structures have proven as efficient candidates as corrosion inhibitors. The corrosion inhibitors in acidic environment affect the corrosion process in a number of ways. It is not possible to assign a single general mechanism of action to an inhibitor, because the mechanism of inhibition of an inhibitor may vary with factors such as concentration, pH, nature of the acid anion, nature of the metal, molecular structure, electron density of the functional group and size of the aromatic and aliphatic moiety of the organic molecule [4]. Few compounds inhibit the corrosion process by forming a film on the metal surface. This film adheres to the surface, creating a barrier between the metal and the corrosive medium. If the surfactant molecule is used as inhibitor, then its ability to interact with the metal is directly related to the critical micelle concentration (CMC). The surfactant reduces the surface tension at the interface between the metal and the solution. This helps in the accumulation of the surfactant molecule at the surface of the metal and influences the corrosion properties [5]. Yet, the inhibitor's mechanism is not known properly. This article explained all the possible types of inhibitors' action mechanisms. In this concern, here an attempt is made to explain the mechanism of corrosion inhibitors adsorption on a steel surface in acidic media.

Inhibitors' action mechanism

In the corrosion studies, the organic compounds are added to acid solutions and metal specimens are immersed in the acid solution for specified hours. The loss in the weight of metal together with unit time is taken as the corrosion rate. The addition of a compound to the corrosive solution brings down the weight loss of metal, thus reducing the corrosion rate. There are many models in literature to explain the inhibitors' action mechanism. According to the well accepted model [21-24], the organic molecules get adsorbed on the corroding metal surface; this adsorption is often a displacement reaction involving removal of adsorbed water molecules from the metal surface, i.e.,



There are four primary modes of adsorption associated with inhibitor molecules at surfaces: electrostatic adsorption (physisorption), π -back bonding, chemisorption, and organometallic complex formation [6]. Furthermore, the stability of the adsorbed organic compound films/layer on the metal surface depends on the nature of functional groups, aromaticity, possible steric factors, electronic density of donors, type of corrosive medium and nature of interaction between its p-orbital with the d-orbital of iron. Basic information on the mode of adsorption of these inhibitor molecules on metal surface can be drawn from the adsorption isotherm. There are several adsorption isotherms like Langmuir, Flory–Huggins, Temkin, Freundlich, and Frumkin, that explain the corrosion-inhibition mechanism [90-92].

$$\text{Langmuir adsorption isotherm: } \frac{C}{\theta} = \frac{1}{K_{ads}} + C$$

$$\text{Flory-Huggins adsorption isotherm: } \log\left(\frac{\theta}{C}\right) = \log(K_{ads}) + a \log(1 - \theta)$$

$$\text{Temkin adsorption isotherm: } \theta = \frac{1}{f} \ln K_{ads} C$$

$$\text{Freundlich adsorption isotherm: } \log \theta = \log K_{ads} + n \log C$$

$$\text{Frumkin adsorption isotherm: } \ln\left(\frac{\theta}{(1-\theta)C}\right) = \ln K_{ads} + 2a\theta$$

where C is the inhibitor concentration, θ is the degree of surface coverage, K_{ads} is the adsorptive equilibrium constant, f is the factor of energetic inhomogeneity, and the parameter 'a' is the number of water molecules replaced by inhibitor molecules on the metal surface.

Adsorption of organic molecules on the metal surface is also influenced by its molecular structure, surface charge density and zero charge potential of metal. The calculation of the surface charge gives an idea of the type of interaction between metal/inhibitor. The surface charge is the position of the corrosion potential E_{corr} with respect to the respective potential of zero charge (E_q). When the difference $E_r = E_{cor} - E_q = 0$ is negative, where E_r is the Antropov "rational" corrosion potential, the electrode surface has a negative net charge and the adsorption of cation is favored, i.e., the cationic form of the inhibitor gets directly adsorbed to steel by replacing protonated water molecule. On the contrary, when E_r becomes positive, the adsorption of anions is favored, hence, anions (Cl^- or SO_4^{2-}) get adsorbed on metal surface, and then interaction with the protonated inhibitor molecule is expected. This condition favors the formation of a film, which prevents the interaction between metal and solution [7]. If E_r is zero, neither cation nor the anion of solution interact with the metal; hence the inhibitor molecule interacts through its $p\pi$ electrons with the empty $d\pi$ orbitals of iron metal.

In recent years, use of quantum chemical techniques like MNDO, AM1, PM3 and many other studies have gained attention as powerful tools in knowing fundamental parameters for adsorption and corrosion inhibition mechanisms. Quantum parameters like frontier orbital energy of HOMO and LUMO, Mulliken charges, ionization energy, electron affinity, hardness, electrophilicity index, back bonding tendency, electrostatic potential map inhibitor, are generators for corrosion study [8-16]. But nowadays, Ab-initio and DFT have become attractive theoretical methods since they give exact basic parameters for even huge complex (multi-electron system) molecules. In the ab-initio, HF calculation, average of Coulombic repulsion between electron-electron is considered for further determination of quantum parameters. DFT uses electronic density as basic parameter in place of electronic wave function. By using sophisticated computational tools and with some basics, HSAB concept (the exact nature of the interactions between a metal surface and an organic molecule depends on the

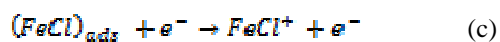
relative coordinating strength towards the metal, and of the particular groups present in the molecule) provides a systematic way for the analysis of the inhibitor/metal interaction. Thus, it is possible to ascertain a suitable mechanism for inhibition process. These techniques in support with electrochemical studies help us to know the inhibitor molecule's mechanism of interaction [17-20].

The actual corrosion inhibition mechanism in acidic (HCl) medium by an inhibitor molecule occurs through the following modes:

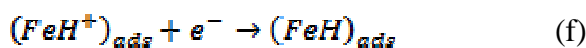
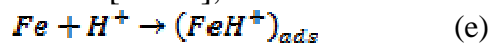
- (a) Electrostatic attraction between the charged molecules and charged metal,
- (b) Interaction of uncharged electron pairs in the molecule with metal,
- (c) Interaction of p-electrons with metal,
- (d) Combination of (a) and (c).

The inhibitor molecule may block anodic or cathodic or both sites and prevents them to undergo metal dissolution or hydrogen evolution reactions. The following mechanism causes metal dissolution and hydrogen evolution process occurred during corrosion.

The metal dissolution occurs through the following reaction pathway from (a) to (d)



Cathodic hydrogen evolution reaction may be given by the reaction pathway from (e) to (g) as given below [25-29],



In this respect an attempt is made to study the mechanism of inhibitor compounds in acidic media. The inhibitors reviewed for mechanistic study are represented in Table 1.

Mechanism of inhibitors studied under different groups

Xanthene group

I.B. Obot and N.O.Obi-Egbedi have investigated [29-32] the effect of xanthene, xanthone and xanthione as corrosion inhibitors in 0.5M sulphuric acid medium. They act as anodic inhibitors preventing anodic metal dissolution by forming metal-ligand complex on to the steel. Adsorption obeys Langmuir adsorption isotherm in xanthone and xanthenes, and Dubinine-Radushkevich adsorption in xanthione. The adsorption of xanthione and xanthone follows first order kinetics, and follows zero order in xanthene.

Table 1. Classification of corrosion inhibitors.

| Class of compounds | Name of compounds | Ref. |
|-------------------------|--|---------------|
| Xanthene compounds | xanthene, xanthone and xanthione | [29-32] |
| Green inhibitors | fig leaves (FL), medicago sativa (MS), mimosa tannin (MT), kalmegh, neem extracts, and nuclea latifolia (NL), ciprofloxacin (CFC), Norfloxacin(NFC), ofloxacin(OFC), sparfloxacin(SFC), Chlorophytum borivilianum root extract (CBRE), Musa paradisiaca peel | [33-39,85,86] |
| Surfactants | Cationic gemini surfactant, 3,5-bis(methylene octadecyl dimethylammonium chloride)-1,2,4-triazole (18-triazole-18) Myristyltrimethylammonium bromide/ chloride (MTABr, MTACL) and Trioctylmethylammonium bromide/chloride (TOMABr, TOMACL), Tween -20 & Tween-40, TRITONX-405, Cetyl trimethylammonium bromide. | [40-45] |
| Acids | glycine, alanine and leucine, indole -3- acetic acid, indole -5- carboxylic acid, 12-aminododecanoic acid. | [46-49] |
| polymers | poly vinyl alcohol-aniline, Polyethylene Glycol Methyl Ether, Polythiophene- β -Naphtholsulphonic acid:, polyethylene amine, polyaniline-co-toulidine, acetyl thiourea chitosan. | [50-54] |
| Nitrogen heterocycles | 2-acetyl pyridine, 2-acetyl pyridine phosphate, (2Z)-3-imino-4-methyl-2-(pyridin-3-ylhydrazono) pentanenitrile(I); 4-(3,4-dichlorophenyl)-2,6-dimethyl-1,2-dihydropyridine-3,5-dicarbonitrile(II); 1,4-diamino-5-cyano-2-(4-methoxyphenyl)-6-oxo-1,6-dihydropyridine-3-carboxylic acid(III); ethyl 4-amino-5-cyano-2-(dicyanomethylene)-6-phenyl-1,2-dihydropyridine-3-carboxylate(IV), 3,5-dimethyl-1H-pyrazole (P1), pyridine (P2) and 2-(3-methyl-1H-pyrazol-5-yl) pyridine (P3), ethyl 5,50-dimethyl-10H-1,30-bipyrazole-3 carboxylate (P1) and 3,5,50-trimethyl-10H-1,30-bipyrazole (P2). | [55-59] |
| Imidazole compounds | 2-aminomethylbenzimidazole, [bis(benzimidazol-2-ylethyl)sulfide, 2,2'-bis(benzimidazole), 2-mercaptoimidazole (2MI), 2-mercaptobenzoimidazole(2MBI), 2-mercapto-5-methylbenzimidazole (2M5MBI) and 2-mercapto-5-nitrobenzimidazole (2M5NBI), 2-mercapto-1-methylimidazole. | [17,60-62] |
| Schiff bases | 3-(4-((Z)-indolin-3-ylideneamino)phenylimino)indolin-2-one Schiff base (PDBI), aminobiphenyl(APh), Aminobiphenyl Schiff base(APh-S), <i>N,N</i> -ortho-phenylene acetyl acetone imine (S1) and 4-[(3-[[1-(2-hydroxy phenyl)methylidene] amino] propyl] ethanemidol]-1,3-benzenediol (S2), 1,3-bis[2-(2-hydroxy benzylideneamino) phenoxy] propane (P1), 1,3-bis[2-(5-chloro-2-hydroxybenzylideneamino) phenoxy] propane(P2), and 1,3-bis[2-(5-bromo-2-hydroxybenzylideneamino) phenoxy] propane(P3), 2-[[[(4-methoxyphenyl)imino]methyl]phenol-SB1 and 1-[[[(4-methoxyphenyl)imino]methyl]-2-naphthol-SB2, benzylidene-pyrimidin-2-yl-amine (A), (4-methyl-benzylidene)-pyrimidine-2-yl-amine (B) and (4-chloro-benzylidene)- pyrimidine-2-yl-amine(C), <i>N,N</i> -bis(salicylidene)-2-hydroxy-1,3-propanediamine (LOH) and <i>N,N</i> -bis(2-hydroxyacetophenylidene)-2-hydroxy-1,3-propanediamine (LACOH) | [25,63-68] |
| Triazole compounds | 3,5-diphenyl-4H-1,2,4-triazole (DHT), 3,5-bis(4-pyridyl)-4H-1,2,4-triazole (4-PHT) and 3,5-bis(4-methylthiophenyl)-4H-1,2,4-triazole, derivatives 5-amino-1,2,4-triazole (5-ATA), 5-amino-3-mercapto-1,2,4-triazole (5-AMT), 5-amino-3-methylthio-1,2,4-triazole (5-AMeTT) or 1-amino-3-methylthio-1,2,4-triazole (1-AMeTT), 1-[2-(4-nitrophenyl)-5-[1,2,4]triazol-1-ylmethyl-[1,3,4]oxadiazol-3-yl]-ethanone (NTOE) and 1-(4-methoxy-phenyl)-2-(5-[1,2,4]triazol-1-ylmethyl-4H-[1,2,4]triazol-3-ylsulfanyl)-ethanone (MTTE), namely triazole, aminotriazole and benzotriazole, (4-chloroacetophenone-O-1-(1,3,4-triazolyl) metheneoxime (CATM), 4-methoxyl-acetophenone-O-1-(1,3,4-triazolyl)-metheneoxime (MATM) and 4-fluoro-acetophenone-O-1-(1,3,4-triazolyl)-metheneoxime (FATM). | [69-74] |
| Miscellaneous compounds | cigerratebut(Cb), 2-(6-methylpyridin-2-yl)-1H-imidazo[4,5-f][1,10]phenanthroline(MIP), Farmazano benzaldehyde (FB), 2-methyl furan, furfuryl alcohol and furfuryl amine, cinnamaldehyde, benzalacetone and chalcone, N-[morpholin-4-yl(phenyl)methyl]acetamide(MPA), 2,5-bis(2-thienyl)-1,3,4-thiadiazole (2-TTH) and 2,5-bis(3-thienyl)-1,3,4-thiadiazole (3-TTH), namely 1-(2,6-diazene)-3-benzyl thiourea (ST1), 1-(3'-pyridyl) - 3 - benzyl thiourea (ST2), 1 - (3' - pyridyl) - 1 - phenyl thiourea (ST3), 1-(2' - pyridyl)-3-phenyl thiourea (ST4), guanine, adenine, 2,6-diaminopurine, 6-thioguanine and 2,6-dithiopurine, 1-octyl-3-methylimidazolium L-prolinate ([Omim]Lpro), 3-amino alkylated indoles (AAIs) namely, N-((1H-indol-3-yl)(phenyl)methyl)-N-ethyl ethanamine (AAI-1), 3-(phenyl(pyrrolidin-1-yl)methyl)-1H-indole (AAI-2) and 3-(phenyl(piperidin-1-yl)methyl)-1H-indole (AAI-3) | [75-84,87,88] |

The inhibition efficiency of the compounds follows the order of Xanthione > Xanthone > Xanthene. This can be explained by considering its chemical structure as in Fig. 1. Xanthione possesses O and S hetero atoms, in xanthone both heteroatoms are O but in case of xanthenes it contain only one O-atom. The inhibition effect of hetero atoms follows the order of S>N>O. In aqueous acidic solutions, the xanthene moiety (XEN) exists either as neutral molecules or in the form of cations (protonated XEN).

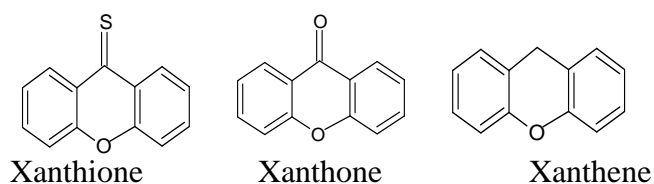


Figure 1. Structure of xanthione, xanthone and xanthene.

Generally, two modes of adsorption could be considered. The neutral XEN may be adsorbed on the metal surface via the chemisorption involving the displacement of water molecules from the metal surface and the sharing of electrons between oxygen atom and iron. The XEN molecules can be adsorbed also on the metal surface on the basis of donor–acceptor interactions between p-electrons of the heterocycle and vacant d-orbitals of iron. On the other hand, SO_4^{2-} could adsorb on the metal surface, then the protonated XEN may be adsorbed through electrostatic interactions between the positive molecules and already adsorbed sulphate ions, thus forming the metal complexes of Fe^{2+} and XEN. These complexes might adsorb onto steel surface by Vander Waals force to form a protective film over the mild steel surface. The same is supported by the frontier orbital calculations. HOMO & LUMO distribution is on an entire molecule, so they interact with steel surface with its hetero atoms and π system forming donor-acceptor type bond, in the case of a neutral molecule. The electronic absorption spectra of XAN in sulphuric acid test solution displayed $\pi \rightarrow \pi^*$ transition. After 3 days of steel immersion in the same test solution, the band maximum underwent a blue shift, suggesting the interaction between XAN and Fe^{2+} ions in the solution. Furthermore, there is an increase in the absorbance of this band. It is clear that there was no significant difference in the shape of the spectra before and after the immersion of XAN, showing a possibility of physisorption or a weak interaction between XAN and mild steel.

Green inhibitors

The plant extracts of fig leaves (FL), medicago sativa (MS), mimosa tannin (MT), kalmegh, neem extracts, and nuclea latifolia (NL) serve as good inhibitors for steel, and their phytochemical components formed stable complex on active sites of the metal, thereby reducing the corrosion rate. Increase in the concentration of the phytochemicals increases the amount of the surface complex, resulting in greater inhibition efficiency. A.M. Al-Turkustani et al.

verified the effect of Medicago Sativa (MS) as inhibitor for steel [35]. MS contains riboflavin, guanine, guanosine, biotin, and cytidine components. So, it contains a number of nitrogen atoms with free electron pair and aromatic electrons through which adsorption occurs onto steel surface, thereby preventing its interaction with corrosive media. Furthermore, MS has a marked effect on pitting corrosion, which was revealed by SEM images. S. Martinez et al. investigated the effect of mimosa tannin (MT) as efficient inhibitor for steel [38]. MT extract was tested in different pH as corrosion inhibitor, and at pH 1 and 2 the flavanoids of MT have formed a cross linked polymeric layer on steel, inhibiting the corrosion due to chemisorptions. At pH-3, the tannin group of MT forms cationic ferric tannate, which gets adsorbed on steel through spatially adsorbed anions through electrostatic interaction, thereby preventing contact of steel with corrosive media. Taleb H. Ibrahim et al. [34] investigated the effect of fig leaves extract on steel corrosion in 2M HCl. It shows very high efficiency of 87%, and was found to obey Langmuir isotherm from which we can say that the phytochemicals of fig leaves form a monolayer over steel, and hence act as a barrier against the corrosion of steel. I.E. Uwah et al. studied [37] the effect of inhibitive action of ethanolic extracts from *Nauclea latifolia* (NL) on steel. Ethanolic extracts of NL [root (RT), bark (BK) and leaves (LV)] revealed the presence of appreciable quantities of flavonoids, polyphenols and glycosides. It has been also detected the presence of alkaloids (in the root and leaves extract) and tannins (in the bark extract). The inhibition efficiency trend is in the order of RT > LV > BK. The leaves and roots extracts show the presence of alkaloids which contain nitrogen, oxygen and aromatic ring in their molecular structures, thus showing higher efficiency. From the observed results, it can be inferred that the insoluble Fe–NL complexes dominate the adsorbed intermediate, and thus the resultant inhibitive effects. Ayssar Nahl et al. investigated [36] neem extract as a corrosion inhibitor for carbon steel in HCl medium. Neem extract contains tannins and a series of complex compounds called “triterpenes” or, more specifically, limonoids as major components. The high inhibition efficiency of neem may be attributed to the presence of tannins, triterpenes, and many other organic compounds. As tannins contain polyphenolic moieties, and these moieties have the ability to form tanninate salts with ferric ions, the corrosion inhibition of tannins is due to the formation of a highly cross-lined network of ferric tanninate salts that protects the metal surface. In the same way, tri-terpenes have some functional groups such as (OH, C = O, C = C) that can interact with the metal surface and protect it from the attack from acid. The adsorption of fig leaves follows Langmuir adsorption forming a layer of monomeric film, thereby protecting the steel from corrosion. Ambrish Singh et al. [33] investigated Kalmegh plant leaves as corrosion inhibitor for steel. Kalmegh leaves extract contains oxygen atoms in functional groups (O–H, C=C, C=O, C–H, C–O) and aromatic ring, which meets the general consideration of typical corrosion inhibitors, as revealed by the FT-IR analysis. Kalmegh leaves extract molecules can also adsorb onto the metal surface on the basis of donor-acceptor interactions between π -electrons of aromatic ring and vacant d-orbitals of Fe. The non-bonded electrons of heteroatoms get protonated in acid media, thus getting

adsorbed on the negatively charged metal surface when protonated. In their turn, when the leaves extract is on the metal surface, a coordinate bond may be formed by partial transference of electrons from the polar atoms (O atoms) onto the metal surface. The leaves extract effect could also be due to the large size of constituent's molecule which covers wide areas on the metal surface, thus producing high inhibition efficiency. Nnabuk. O. Eddy et al. [39] studied some fluoroquinolones, namely ciprofloxacin (CFC), norfloxacin(NFC), ofloxacin(OFC), sparfloxacin(SFC) as corrosion inhibitors for mild steel in H₂SO₄. These are antimalarial drugs, hence they are environmental friendly inhibitors. The inhibition efficiency follows the order of OFC > NFC > CFC > SFC, and they undergo physical adsorption, obeying Langmuir adsorption. The adsorption site calculated from quantum mechanical parameters reveals that in CFC and NFC, the ring containing Cl and O atoms, in SFC - N3 atom and in OFC N4 atom of piperazine ring attached directly to the metal surface. In addition to the donation of π - electrons to metal, the inhibitor accepts electrons from metal to π^* orbital forming feedback bonding, suggesting comprehensive adsorption of the inhibitor, thus controlling metal dissolution or anodic process. Gopal Ji et al. [85] studied the inhibition effect of aqueous Chlorophytum borivilianum root extract (CBRE) on mild steel corrosion in 1 M HCl and 0.5 M H₂SO₄. The CBRE shows inhibition efficiency of 90% in 1 M HCl, and 85 % in 0.5 M H₂SO₄ media. The CBRE gets adsorbed on active sites of steel, and thus inhibits its corrosion. The adsorption of CBRE obeys Langmuir isotherm in both cases. The CBRE's mechanism of action can be explained on the basis of molecular interaction of the inhibitor with mild steel. CBRE contains saponins as major constituents. Saponins are the class of chemical compounds which contain a number of fused rings, possessing several O atoms and -OH functional group in their structure. CBRE, in addition to saponins, contains other phyto-chemicals like tannins and flavanoids, which are rich with aromatic rings and heterocycles. The structure assists in the adsorption of CBRE on mild steel. The CBRE layer at the acid-steel interface is formed either due to chemisorption by forming chemical bond between π electrons or lone pair electrons (from N, O atoms or aromatic rings of organic moieties) and vacant d-orbital electrons of iron. It also may be due to physisorption, in which protonated organic moieties of CBRE interact with Fe²⁺ via bridging chloride ions/ sulfate ions (being adsorbed on a steel surface) to make metal inhibitor complexes with a weak electrostatic interaction. Gopal Ji et al. [86] investigated the effect of aqueous extract of Musa paradisiaca peel on the corrosion inhibition of mild steel in 1 M HCl. The authors also verified the changes in the inhibition effect with the ripening of peel. The Musa paradisiaca peel extract impedes the corrosion of mild steel in 1M HCl for several hours. The Musa paradisiaca peel raw extract contains galocatechin moiety and ripened peel extract possesses catechin moiety, as confirmed by HPLC. From the results of the various techniques, it could be acknowledged that the corrosion of mild steel is minimized by the significant adsorption of the organic moieties of the extracts. Hence, we can say that, in real sense, the corrosion inhibition mechanism is purely an adsorption mechanism. The charge on steel surface plays a prominent role in assigning the possible mechanism for corrosion.

From literature reviews, steel surface is positively charged in acid media. Gallocatechin and catechin have tendency to get protonated in acid solutions. These positively charged species physically adsorb onto metal surface via electrostatic coupling. Structurally, gallocatechin and catechin molecules contain several π electrons on benzene rings and non-bonding electrons on oxygen atom, which assist in formation of a chemical bond with vacant d-orbital electrons of charged steel surface. The adsorption of molecules cover the effective surface area of mild steel, and retard the rate of corrosion either physically or chemically or both. However, the exact mechanism of corrosion inhibition (physical/chemical) could not be envisaged, due to unspecified molecular weight of the extracts.

Surfactants

The inhibitory action of the surfactant is of adsorption type; all surfactant molecules follow the same type of mechanism. The hydrophilic head group interacts with steel surface, while the hydrophobic tail group spreads in aqueous corrosive media. Furthermore, the efficiency of the surfactant inhibitor increases with increasing hydrophobic chain length. This is because an increase in the chain length increases adsorptive power and surface activity of the inhibitor, which in turn increases surface coverage, which is expressed in θ . Ling-Guang Qiu et al. investigated the effect of triazole-based cationic Gemini surfactant, 3,5-bis(methylene octadecyl dimethyl-ammonium chloride)-1,2,4-triazole (18-triazole-18) in 1M HCl [40]. This surfactant prevents the corrosion by forming a stable monolayer film, and its adsorption characteristics obey Langmuir isotherm. The 18-triazole-18 utilizes its four nitrogen atoms – two on triazole ring and two on ammonium alkyl chain – to get bind to steel surface through interhydrophobic interaction (as in Fig. 2).

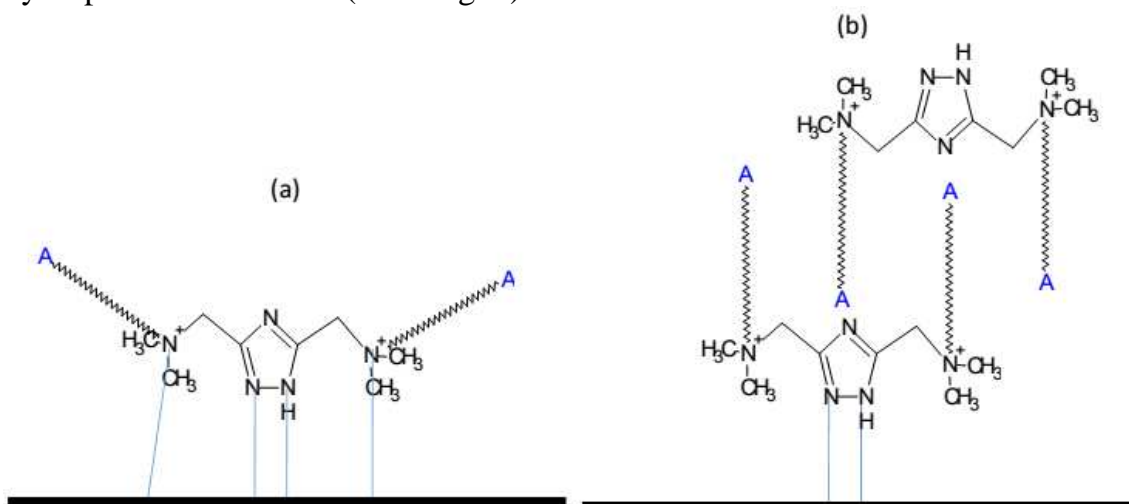


Figure 2. Representation of adsorption of surfactant 18-triazole-18 on steel before CMC (a) and after CMC (b).

The variation in the inhibition efficiency above CMC is quite small; this is because, above CMC, the quaternary ammonium nitrogen gets desorbed from the surface; however, triazole nitrogens are still in interaction with steel. Thereafter,

an increase in the concentration of surfactant above CMC leads to the formation of a multilayer film on steel. R. Fuchs-Godec et al. studied [42] the action of *N*-alkyl quaternary ammonium salts as inhibitors. *N*-alkyl quaternary ammonium salts, like myristyltrimethylammonium bromide/ chloride (MTABr, MTACl) and trioctylmethylammonium bromide/chloride (TOMABr, TOMACl) surfactants used in this study, acted as mixed type inhibitors causing the retardation of the corrosion reactions.

It follows Flory-Huggins adsorption isotherm. The inhibition effect of the same surfactant with Br⁻ counter ion is higher than the corresponding Cl⁻ ions. Moreover, surfactants, which have Br⁻, as counter ion, have smaller CMC values than the identical type of surfactant with Cl⁻ counter ions. This is because Cl⁻ ion is more solvated in solution, thereby preventing its interaction with the cationic surfactant head group, and hence causing the repulsion between cationic head groups within the surfactant and also in surfactant micelle. It acts as mixed inhibitor controlling both anodic and cathodic corrosion reaction by forming an adsorption film over the entire surface. Mukta Sharma et al. studied the effect of cetyl trimethylammonium bromide as an inhibitor for steel corrosion. The adsorption of cetyl trimethylammonium bromide obeys Langmuir adsorption and behaves as mixed inhibitor [41]. Xianghong Li and Guannan Mu studied [43-44] the effect of tween-40 and tween-20 on cold rolled steel. The adsorption of both tween-20 and tween-40 on steel obeys Langmuir adsorption and both of them act as cathodic inhibitor. They reduce the surface roughness of steel on their adsorption. R. Fuchs-Godec investigated [45] the inhibitory action of triton-X-405 on steel. The adsorption of non-ionic surfactants of TRITON-X series type on stainless steel in 2 M sulphuric acid obeys the Flory-Huggins adsorption model. The ΔG_{ads} values, calculated using the Flory-Huggins adsorption model, suggest the chemisorption mechanism. The higher inhibition efficiency of TRITON-X-405 at lower concentrations ($C_{inh} < CMC$) in comparison with TRITON-X-100 is due to the large size of the head group (TRITON-X-100, 9–10 ethylene oxide groups and TRITONX-405 around 40 ethylene oxide groups), which lies flat on the surface. But these excellent inhibition properties of TRITON-X-405 are valid only in the cathodic range up to the corrosion potential and at low anodic over potentials while the desorption process is in progress. Desorption of the protective layer was formed in the presence of TRITON-X-405, since it creates a more porous and lower-grade film.

Amino acids and organic acids

Since amino acids are nontoxic, economically viable and easily available, H. Ashassi-Sorkhabi et al. [46] studied three amino acids, namely glycine, alanine and leucine as corrosion inhibitors for mild steel. The amino acids interact with the steel surface through its N- atoms and –COO group forming a compact barrier complex between steel and corrosive media. The adsorption of an amino acid on the steel surface generally follows Langmuir isotherm. Glycine and alanine behave as a mixed inhibitor controlling both anodic corrosion and cathodic hydrogen evolution process. Whereas leucine behaves as a cathodic

inhibitor, acetic acid acts as a mixed inhibitor and Gulsen Auci [47] used indole -3- acetic acid as a corrosion inhibitor for mild steel in HCl medium.

The inhibitor utilizes its π electrons and non-bonding electrons of nitrogen (indole moiety) along with $-\text{COO}$ group to get adsorbed onto steel, forming a film. The adsorption characteristics of the compounds obey Langmuir adsorption, and Gibbs free energy calculations reveal that it undergoes a comprehensive adsorption. G. Quartaone et al. [48] investigated indole -5- carboxylic acid as steel corrosion inhibitor. Steel is positively charged (form PZC), and indole-5- carboxylic acid is a polar molecule. There exists electrostatic interaction between polar $-\text{COOH}$ group and steel surface. 12-aminododecanoic acid (AA) is investigated as corrosion inhibitor for steel by Saad Ghareba et al. [49]. It acts as mixed inhibitor controlling the anodic process to a larger extent. The adsorption of AA on steel obeys Langmuir adsorption forming a monolayer, preventing mass transfer. The formation of an AA monolayer is confirmed by the PM-IRRAS. The adsorption mechanism (Tables 2 and 3) occurs through acid base reaction with the $-\text{COOH}$ group and the Fe^{+2} forming surface salt. The $-\text{NH}_2$ group protonated in acid solution is directly attached to the cathodic site on steel preventing hydrogen evolution.

Table 2. Corrosion inhibitors following adsorption mechanism in H_2SO_4 medium.

| Inhibitor | Medium | % IE | Type of inhibitor |
|--|--|------|-------------------|
| Xanthione | $\text{H}_2\text{SO}_4(0.5 \text{ M})$ | 98 | Anodic |
| <i>N, N</i> -ethylen-bis (salicylideneimine) | $\text{H}_2\text{SO}_4(0.5 \text{ M})$ | 98 | Mixed |
| <i>N, N</i> -isopropylen-bis (salicylideneimine) | $\text{H}_2\text{SO}_4(0.5 \text{ M})$ | 98 | Mixed |
| <i>N</i> -acetylacetoneimine, <i>N</i> -(2-hydroxybenzophenoneimine) <i>ortho</i> -phenylene | $\text{H}_2\text{SO}_4(0.5 \text{ M})$ | 97 | Mixed |
| 2,5-bis(3-thienyl)-1,3,4-thiadiazole | $\text{H}_2\text{SO}_4(0.5 \text{ M})$ | 95 | Mixed |
| Xanthone | $\text{H}_2\text{SO}_4(0.5 \text{ M})$ | 93 | Anodic |
| 2,5-bis(2-thienyl)-1,3,4-thiadiazole | $\text{H}_2\text{SO}_4(0.5 \text{ M})$ | 91 | Mixed |
| Xanthenes | $\text{H}_2\text{SO}_4(0.5 \text{ M})$ | 90 | Anodic |
| Chlorophytum borivilianum root extract | $\text{H}_2\text{SO}_4(0.5 \text{ M})$ | 85 | Mixed |
| diethyl pyrazine-2,3-dicarboxylate | $\text{H}_2\text{SO}_4(0.5 \text{ M})$ | 82 | Cathodic |
| 1-octyl-3-methylimidazolium L-prolinate ([Omim]Lpro), | $\text{H}_2\text{SO}_4(0.5 \text{ M})$ | 80 | Cathodic |
| 2-(6-methylpyridin-2-yl)-1H-imidazo [4,5-f][1,10] phenanthroline | $\text{H}_2\text{SO}_4(0.5 \text{ M})$ | 72 | Cathodic |
| 2-mercaptoimidazole | $\text{H}_2\text{SO}_4(1 \text{ M})$ | 98 | Mixed |
| Tween -40 | $\text{H}_2\text{SO}_4(1 \text{ M})$ | 95 | Cathodic |
| Nauclea latifolia | $\text{H}_2\text{SO}_4(1 \text{ M})$ | 94 | Anodic |
| TRITON-X-405 | $\text{H}_2\text{SO}_4(1 \text{ M})$ | 90 | Mixed |
| Tween -20 | $\text{H}_2\text{SO}_4(1 \text{ M})$ | 76 | Cathodic |
| 2-Mercapto-1-methylimidazole | $\text{H}_2\text{SO}_4(2 \text{ M})$ | 98 | Anodic |
| Medicago Sativa | $\text{H}_2\text{SO}_4(2 \text{ M})$ | 90 | Mixed |
| <i>n</i> -alkyl quaternary ammonium salts | $\text{H}_2\text{SO}_4(2 \text{ M})$ | | Mixed |
| Mimosa tannin | $\text{H}_2\text{SO}_4(\text{M})$ | 87 | Mixed |

Polymers

The polymeric substances are proved to be an efficient inhibitor for mild steel, since they possess high molecular weight, and they have capability to form a complex with metals, which has a larger surface area and a higher surface coverage power, forming a compact barrier film on the metal surface. The polymeric inhibitors studied here are poly vinyl alcohol-aniline, PEGME, PTh β -NSA, polyethylene amine, polyaniline-co-toulidine, acetyl thiourea chitosan, and serve as mixed inhibitors for steel, controlling both anodic dissolution and cathodic hydrogen evolution reactions simultaneously. The polymeric substance undergoes protonation in acidic solution, and the protonated molecule gets adsorbed onto the cathodic site of steel, thereby controlling the cathodic reaction and anodic adsorption that take place through π -electrons of the aromatic ring and lone pair electrons on heteroatoms of the molecule, forming a compact barrier film that, thus, prevents the interaction of steel with the corrosive environment. M. Mobin and N. Tanveer studied [51] the corrosion inhibitive effect of polyaniline co-toluidine coating of steel in different corrosive media. The polymeric film is stable even after 30 days of immersion, as revealed by its electrochemical parameters, and it shows 78% inhibition efficiency in HCl. The adsorbed film obeys Langmuir adsorption isotherm. A.K. Dubey et al. investigated [53] the corrosion inhibitive effect of PEGME on steel. PEGME, at higher temperature and at higher concentrations, exerts a greater influence on the cathodic process than on the anodic process. PEGME molecules interact with the metal surface through the oxygen and nitrogen lone pair of electrons, or by forming intermediate species $(M-In)_{ads}$, or $(M-In-OH)_{ads}$ or $(M-H-In)_{ads}$, which prevent contact of steel with corrosive media. R. Karthikaiselvi et al. studied [50] the effect of poly vinyl alcohol-aniline on corrosion of steel. The inhibitory action of poly vinyl alcohol-aniline is due to its interaction on anodic sites, which occurs through p-electrons of aromatic rings and a lone pair of electrons of the nitrogen atom, which decreases the anodic dissolution. The protonated species of polymer adsorb onto the cathodic sites of the steel decrease, thereby minimizing hydrogen evolution. The high performance of the poly vinyl alcohol-aniline polymer is attributed to the presence of π electrons, and quaternary nitrogen atom and its larger molecular size. A.M. Fekry et al. studied [54] the inhibitive effect of acetyl thiourea chitosan on mild steel, and concluded it provides protection of about 94.5%, due to the homogeneous polymer composite film polymer/metal interphase, which acts like a barrier between steel and corrosive media. The acetyl thiourea chitosan possesses $-OH$, $-C=S$ and $-NH$ groups which can interact with the steel with its lone pair of electrons on heteroatoms, forming a layer of stable polymeric film, which protects steel from corrosion. V. Suresh Kumar et al. studied [52] the inhibitory effect of polythiophene- β -naphtholsulphonic acid (PTh-NSA) on steel. The polymeric inhibitor PTh-NSA could be adsorbed onto the metal surface via the lone pair of electrons present on its nitrogen atoms.

Table 3. Corrosion inhibitors following adsorption mechanism in HCl medium.

| Name of inhibitor | Medium | % IE | Type of inhibitor |
|--|------------|--------------------|-------------------|
| 5-amino-3-mercapto-1,2,4-triazole | HCl(0.1 M) | 95 | Mixed |
| <i>polythiophene-_n-naphtholsulphonic acid</i> | HCl(0.1 M) | 95 | Mixed |
| Leucine | HCl(0.1 M) | 91.64 | cathodic |
| 1,3-bis[2-(2-hydroxy benzylidenamino) phenoxy] propane | HCl(0.1 M) | 89 | Mixed |
| 5-amino-3-methylthio-1,2,4-triazole | HCl(0.1 M) | 86 | Mixed |
| 1,3-bis[2-(5-bromo-2-hydroxybenzylidenamino) phenoxy] propane | HCl(0.1 M) | 85 | Cathodic |
| 1-amino-3-methylthio-1,2,4-triazole | HCl(0.1 M) | 84 | Mixed |
| 1,3-bis[2-(5-chloro-2-hydroxybenzylidenamino) phenoxy] propane | HCl(0.1 M) | 81 | Cathodic |
| Alanine | HCl(0.1 M) | 80.22 | Mixed |
| Glycine | HCl(0.1 M) | 78.95 | Mixed |
| poly(aniline-co-o-toluidine) | HCl(0.1 M) | 78 | Mixed |
| 2-acetyl pyridine phosphate(APP) | HCl(0.1 M) | 53.62 | Mixed |
| 2-acetyl pyridine(ACP) | HCl(0.1 M) | 52.80 | Mixed |
| hydroxybenzylideneamino)biphenyl (Aph-S) | HCl(0.5 M) | 97.2 | Mixed |
| [bis(benzimidazol-2-ylethyl)sulfide | HCl(0.5 M) | 97 | Mixed |
| indole -3- aceticacid | HCl(0.5 M) | 94 | Mixed |
| indole -5- carboxylic acid | HCl(0.5 M) | 93 | Mixed |
| aminobiphenyl (Aph) | HCl(0.5 M) | 92.6 | Cathodic |
| 2-aminomethylbenzimidazole | HCl(0.5 M) | 84 | Cathodic |
| benzylidene-pyrimidin-2-yl-amine | HCl(1 M) | 99 | Mixed |
| (4-methyl-benzylidene)-pyrimidine-2-yl-amine | HCl(1 M) | 99 | Mixed |
| (4-chloro-benzylidene)-pyrimidine-2-yl-amine | HCl(1 M) | 99 | Mixed |
| 1-(4-methoxy-phenyl)-2-(5-[1,2,4]triazol-1-ylmethyl-4H-[1,2,4]triazol-3-ylsulfanyl)-ethanone | HCl(1 M) | 99 | Mixed |
| (4-chloro-acetophenone-O-1-(1,3,4-triazolyl)-metheneoxime | HCl(1 M) | 98 | Mixed |
| Kalmegh (<i>Andrographispaniculata</i>) | HCl(1 M) | 98 | mixed |
| 3,5-bis(methylene octadecyl dimethylammonium chloride)-1,2,4-triazole | HCl(1 M) | 98 | Mixed |
| 3-(phenyl(piperidin-1-yl)methyl)-1H-indole (AAI-3) | HCl(1 M) | 97.8 | Cathodic |
| 3-(phenyl(pyrrolidin-1-yl)methyl)-1H-indole (AAI-2) | HCl(1 M) | 95 | Cathodic |
| 2,2'-bis(benzimidazole) | HCl(1 M) | 95.6 | Mixed |
| 3-(4-((Z)-indolin-3-ylideneamino)phenylimino)indolin-2-one | HCl(1 M) | 95 | Mixed |
| 4-methoxyl-acetophenone-O-1-(1,3,4-triazolyl)-metheneoxime | HCl(1 M) | 94 | Mixed |
| 4-fluoro-acetophenone-O-1-(1,3,4-triazolyl)-metheneoxime | HCl(1 M) | 94 | Mixed |
| (5-methyl-1-pyridin-2-yl-1H-pyrazol-3-yl)methanol | HCl(1 M) | 94 | Cathodic |
| N-((1H-indol-3-yl)(phenyl)methyl)-N-ethyl ethanamine (AAI-1) | HCl(1 M) | 93 | Cathodic |
| furfuryl alcohol | HCl(1 M) | 92.4 | Mixed |
| Triazole | HCl(1 M) | 92 | Mixed |
| N-[morpholin-4-yl(phenyl)methyl]acetamide | HCl(1 M) | 91 | Cathodic |
| Chlorophytum borivilianum root extract | HCl(1 M) | 90 | Mixed |
| Musa paradisiaca peel | HCl(1 M) | 90 | Mixed |
| Neem(<i>Azadirachta indica</i>) | HCl(1 M) | 89 | Mixed |
| 2-(3-methyl-1H-pyrazol-5-yl) pyridine | | | |
| ethyl 5-methyl-1-pyridin-2-yl-1H-pyrazol-3-carboxylate | HCl(1 M) | 87 | Cathodic |
| Benztotriazole | HCl(1 M) | 87 | Mixed |
| Poly (vinyl alcohol – aniline) | HCl(1 M) | 86 | mixed |
| furfuryl amine | HCl(1 M) | 85.8 | Mixed |
| 2- methyl furan | HCl(1 M) | 84.6 | Mixed |
| <i>N,N</i> - <i>ortho</i> -phenylenacetyl acetone imine | HCl(1 M) | 82 | Anodic |
| 4-[(3-/[1-(2-hydroxy phenyl)methylidene] amino/ propyl] ethanemidol]-1,3-benzenediol | HCl(1 M) | 53 | Anodic |
| Farmazanof benzaldehyde | HCl(1 M) | 67.7 | Mixed |
| 3,5-dimethyl-1H-pyrazole | HCl(1 M) | 39 | |
| Pyridine | HCl(1 M) | 21 | |
| Cinnamaldehyde | HCl(5%) | - | Anodic |
| Benzalacetone | HCl(5%) | - | Anodic |
| Chalcone | HCl(5%) | - | Mixed |
| Fig leave | HCl(2 M) | 87 | Mixed |
| Ciggaate buts(aerobic & anaerobic) | HCl(20%) | 84(anae) 92(ae) | Mixed |

The inhibitor might have been adsorbed onto the surface of steel, forming a compact protective thin layer film that acts as a barrier for mass and charge transfers, protecting the steel surface from the attack of the acid solution's aggressive ions. The degree of protection was higher with the increasing of the surface fraction occupied by the adsorbed molecules.

Nitrogen heterocycles

Pyridine, pyrazine and pyrazoles are from the class of nitrogen, containing heterocycles possessing high inhibition efficiency. The inhibition is mainly due to an adsorptive phenomenon. Pyridine contains six membered heterocycles with N-atoms in their ring, pyrazine possesses two N atoms in six member rings, whereas pyrazole is a five membered heterocycles with two N-atoms. These compounds get bound to the steel through the lone pair electrons of nitrogen and the π -electrons of the aromatic ring. This is proved by the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions UV-Visible spectrum. In addition to these bonds, the inhibitor forms feedback bonds by accepting electrons from metal. Ita Bi et al. studied [55] the pyridine derivatives namely, 2-acetyl pyridine (ACP) and 2-acetyl pyridine phosphate (APP) as corrosion inhibitors for mild steel in HCl average, at two different temperatures. Both ACP and APP obey Langmuir adsorption. APP serves as a better inhibitor than ACP. This can be explained with its structure, because ACP contains only two coordinated sites, i.e., one is N-hetero atom of the Py-ring, other is O-atom of acetyl ring, whereas APP possesses one additional coordinated site at the phosphate group. So, APP possesses higher coverage power than ACP. Hence, APP inhibits better when compared to ACP. Through this adsorption site, ACP and APP are chemically adsorbed onto steel through a coordinate bond between inhibitor and metal. The four derivatives of pyridine were studied by S.A. Abd El-Maksoud and A.S. Fouda [59]. They are: (2Z)-3-imino-4-methyl-2-(pyridin-3-ylhydrazono) pentane nitrile(I); 4-(3,4-dichlorophenyl)-2,6-dimethyl-1,2-dihydropyridine-3,5-dicarbonitrile(II); 1,4-diamino-5-cyano-2-(4-methoxyphenyl)-6-oxo-1,6-dihydropyridine-3-carboxylic acid(III); ethyl 4-amino-5-cyano-2-(dicyanomethylene)-6-phenyl-1,2-dihydropyridine-3-carboxylate(IV). The compounds inhibit corrosion by their adsorption onto the steel surface. The adsorption of these compounds on steel follows Langmuir isotherm, and inhibition efficiency follows the order $IV > III > II > I$. Compound IV shows the greatest inhibition among investigated compounds. This may be due to its higher molecular weight – because of the presence of three cyano groups, and the carboxylic ester group which are electron-withdrawing, and to the delocalization of π -orbital on the phenyl group attached directly to the pyridine ring, which disturbs the electron density on the NH of the dihydropyridine. Therefore, the compound IV can easily interact with the already adsorbed Cl^- ions on the steel surface. Compound III has two NH_2 groups which are electron-donating groups, and one cyano group that makes the electron density on the pyridine's nitrogen atom higher than the previous case. But its interaction with adsorbed Cl^- ions is weaker when compared to the compound IV, and its direct interaction with the bare steel is hindered by its bulkier structure. Although in compound II there are two cyano groups which may decrease the

electron density on the nitrogen atom, the presence of two methyl groups which are electron donating increases electronic density on pyridine ring. However, its interaction with steel is prevented due to the presence of two methyl groups at ortho position towards pyridine nitrogen. Compound I is the weakest one in the order of inhibition efficiency among the investigated compounds, which may be due to its lowest molecular weight. Diethyl ester of pyrazine was verified as an inhibitor by M. Bouklah et al. [58], as it contains both nitrogen and oxygen atoms, which assist in adsorption onto steel, and it obeys Langmuir adsorption. The inhibitor's action mechanism is explained with the aid of IR data. Before the immersion of the steel plate the inhibitive solution shows that the major characteristic bands were at 2900 cm^{-1} CH of pyrazine ring, at 2800 and 2760 cm^{-1} for carboxylic CH_2 and CH_3 bands, respectively, for C=O at 1600 cm^{-1} and for C–O at 1540 cm^{-1} . After the immersion of steel a yellow film formed on steel surface, due to the inhibitor deposition, and this has been verified through the IR spectra of the deposit, which shows an absence of the majority of the group bands of pyrazine. This is attributed to the interaction of steel with N and O atoms of the pyrazine derivative. The inhibitive effect of three compounds including 3,5-dimethyl-1H-pyrazole (P1), pyridine (P2) and 2-(3-methyl-1H-pyrazol-5-yl) pyridine (P3) against steel corrosion has been investigated by Hongfang Ma et al. [56] through Ab-initio calculation method. The inhibitive effect of these compounds follows the order $\text{P3} > \text{P1} > \text{P2}$, as verified by experimental results. The quantum data also support the same trend; among them, P3 has a large value of HOMO energy, and a smaller value of ΔE , which is indicative of the higher efficiency of the molecule. As the author has determined from quantum calculations, the reactive centers of P1, P2 and P3 are 3N, 8N, and 13N, respectively. The 3N of P1 is more active than 14N because of its C=N bond. The P1 and P2 molecules are in the same plane with Fe atom. But P3's adsorption structure is different, because there are two rings in its molecule, which are not in one plane. In P3 system, the adsorption of these rings is accompanied by some spatial volume resistance. The bond distance from the adsorptive site is also determined for P3, and it is larger due to existence of special volume resistance. In spite of its larger bond distance, it shows high inhibition efficiency. K. Tebbji et al. have investigated [57] the effect of two pyrazole-type organic compounds, namely ethyl 5,50-dimethyl-10H-1,30-bipyrazole-3 carboxylate (P1) and 3,5,50-trimethyl-10H-1,30-bipyrazole (P2), which were verified as inhibitors for steel corrosion in 1 M HCl media. The experimental results showed that P2 acts as better inhibitor than P1. The group $-\text{COOC}_2\text{H}_5$ in P1 decreases the electronic density on bipyrazole ring. In P2 the $-\text{COO C}_2\text{H}_5$ by $-\text{CH}_3$ group increases the electronic density on bipyrazole, and hence, has higher efficiency. The adsorption of P2 on steel surface is shown below in Fig. 3.

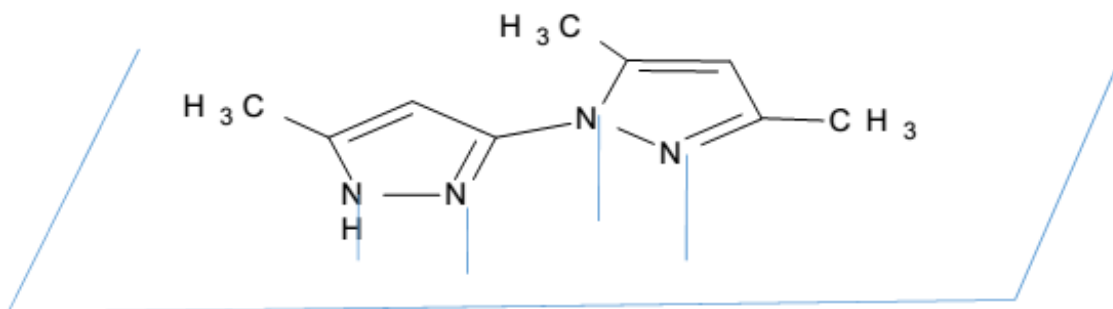


Figure 3. Representation of adsorption of bipyrazole on steel.

Imidazole compounds

The anti-corrosive process of (2-aminomethylbenzimidazole) AMB and [bis(benzimidazol-2-ylethyl)sulfide] BBES was evaluated by J. Cruz et al. [17]. The EIS and polarization resistance studies have indicated that AMB behaves as a cathodic inhibitor controlling cathodic H_2 evolution, while BBES functions as a mixed inhibitor controlling both anodic metal dissolution and cathodic hydrogen evolution. Furthermore, BBES, with two benzimidazole rings, acts as an exceptionally good inhibitor, and forms a multilayer over metal surface. This process is explained by considering theoretical calculations in a more appropriate way. AMB produces more stable conformation only when the protonation takes place at nitrogen (N1). However, for BBES, one stable BBESH form only resulted as protonation occurs at the aromatic N(1). The Mullikan charge values reveal that the imidazole ring becomes symmetrical, which leads to a delocalization region around N1–C2–N3. Therefore, both protonated AMB and BBES generate an electronic delocalization around N1–C2–N3; the conjugate systems N1–C2–N3 and benzene ring present in both AMB and BBES are considered as active sites for the inhibition process. Additionally, the thioether sulfur present in BBES also contributes further to chemical adsorption; thus, BBES behaves as an efficient corrosion inhibitor. Abboud et al. [60] synthesized 2,2'-bis(benzimidazole) and studied its corrosion inhibition action. BBI controls both cathodic and anodic reaction process. BBI is dimer of benzimidazole. Benzimidazole is a “bicycle” system consisting of a five-membered imidazole ring fused with benzene ring. It has two nitrogen atoms: “pyrrolic” nitrogen or N- atom at the 5-position in the molecule, whose lone pair of electrons takes part in the π - system imidazole ring, and “pyridyne” nitrogen or N- atom at the 6-position in the molecule, whose unshared electron pair remains free. So, the pyridyne N- atom acts as an electron donor in the BBI molecule. BBI has an organic base and it protonates in acid solution to form cations. In neutral BBI, adsorption occurs by sharing of lone pair of electrons between nitrogen and the metal surface. In protonated BBI, this is coordinated through negatively charged Cl^- on the metal surface. If the metal surface is positively charged with respect to the potential of zero charge (PZC), the chloride ions will first be adsorbed on the metal surface, which attracts the protonated BBI and protonated water molecules. Thus, a close packed triple layer will form on the metal surface and inhibits the entry of iron ions to the solution, as seen in (a) of Fig. 4. If the metal surface is

negatively charged with respect to the PZC, the protonated water molecules and the protonated forms of BBI are directly adsorbed on the metal surface, as seen in (b) of Fig. 4. When the metal surface attains the potential, it becomes zero with respect to PZC, and neutral BBI molecules are adsorbed through their aromatic π -orbitals on the metal surface, as reported in [60]. The chemical compounds 2-mercaptoimidazole (2MI), 2-mercaptobenzoimidazole (2MBI), 2-mercapto-5-methylbenzimidazole (2M5MBI) and 2-mercapto-5-nitrobenzimidazole (2M5NBI), were studied as inhibitors by R. Álvarez-Bustamante et al. [61] in 1 M H_2SO_4 solution, and have shown good inhibition efficiency. The inhibition efficiency follows the order of $2\text{MI} > 2\text{MBI} > 2\text{M5MBI} > 2\text{M5NBI}$. The adsorption of these compounds onto steel obeys Langmuir adsorption. It is shown that this compound can affect both anodic and cathodic processes. Therefore, it can be classified as a mixed-type inhibitor. However, from variation of both corrosion potential and polarization resistance with [2MI] it was possible to state that the anodic reaction rate of the corrosion process decreases at a greater proportion than the cathodic one. Benali Omar et al. have verified [62] 2-mercapto 1-methyl imidazole as an adsorption inhibitor, which forms an adherent film on the entire steel surface, thus preventing the interaction of steel with the corrosive environment. The adsorption of the inhibitor obeys Langmuir adsorption model, and the thermodynamic parameters reveal the formation of chemisorptions of the inhibitor on steel. E. Gutiérrez et al. [89] have evaluated the inhibition effect and its QSAR properties of fifteen molecules derivated from imidazole and benzimidazole on carbon steel (CS) in 1 M HCl. The authors proposed a predictive model: according to it, the inhibition effect of the molecules varies with the molecules' volume, charge, electronegativity, and aromaticity. The adsorption of these molecules on CS obeys Langmuir isotherm model. The interaction of these molecules with CS is due to the lone pairs of electrons of nitrogen atoms, π -electrons in each one of these compounds, and the vacant d-orbitals of iron surface atoms. The imidazole and benzimidazole derivatives exist in the form of either neutral or cationic molecules in acidic media. In the form of neutral molecules, they can interact with CS by forming coordinate bonds between molecules and Fe atoms. In the cationic form, molecular adsorption is predominantly an electrostatic interaction between the protonated compounds and the negatively charged steel surface resulted from chloride ions adsorption. The adsorption of imidazole and benzimidazole on CS (Fe atom) occurs through the iminic nitrogen and aromatic electron present on their molecular structure. The same is also proved by their theoretical. Further, the quantum molecular parameters, as determined from DFT and calculated $p \rightarrow d$ charge transfer (molecule \rightarrow surface), for imidazole (0.74) and benzimidazole (0.99), have also supported the existence of the heterocycle/Fe interaction.

Schiff bases

Schiff bases (SB) of different organic compounds are proved as efficient inhibitors for preventing corrosion of mild steel. Schiff bases mainly possess ($\text{C}=\text{N}$) group in which N atom gets bind to the steel surface. Moreover, SB undergo protonation in acid solution, and the protonated molecule gets adsorbed

on to the anodic site of steel via the pre adsorbed Cl^- ions. These protonated SB get directly adsorbed onto the cathodic site of steel, in competition with H^+ ions. The inhibition effect of 3-(4-((Z)-indolin-3-ylideneamino) phenylimino)indolin-2-one Schiff base (PDBI) on mild steel is studied, and adsorption of PDBI obeys Langmuir adsorption model [25] (Fig. 5). The adsorption of PDBI occurs through the donor-acceptor interactions between free electron pairs of heteroatoms and π -electrons of multiple bonds, as well as phenyl group and vacant d-orbitals of iron. The skeletal representation of the PDBI molecule's adsorption onto the mild steel surface is presented. The adsorption of heterocyclic compounds occurs when the aromatic rings are normal towards the metal surface, however, parallel, in very few cases.

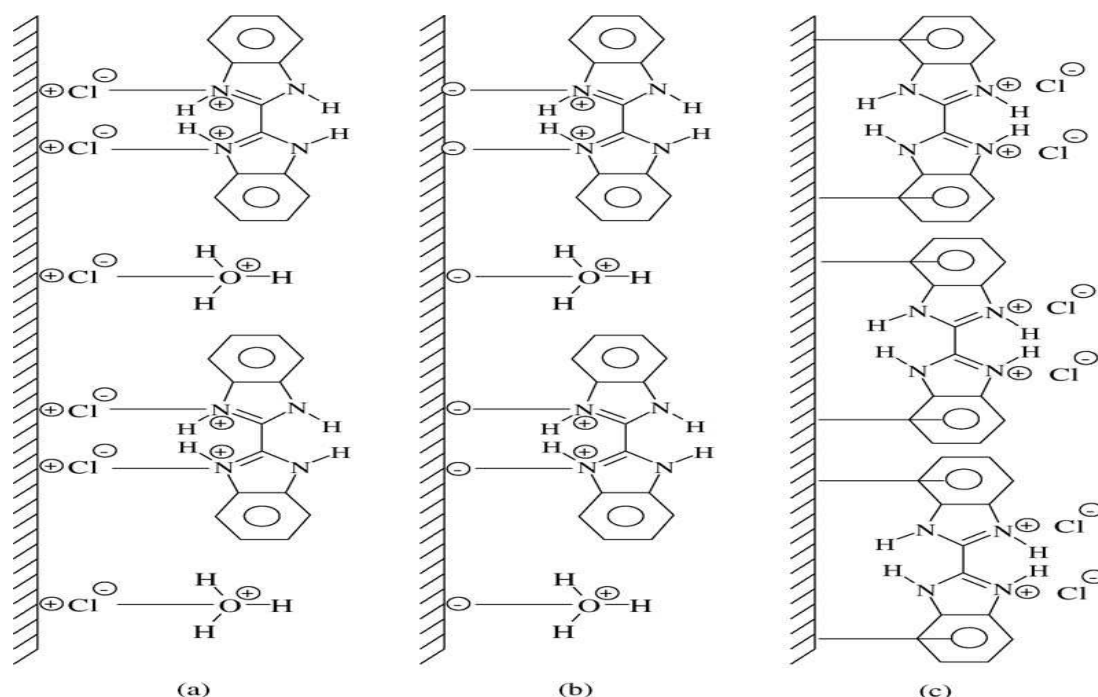


Figure 4. Adsorption model of BBI in accordance with PZC on steel (from ref. 60).

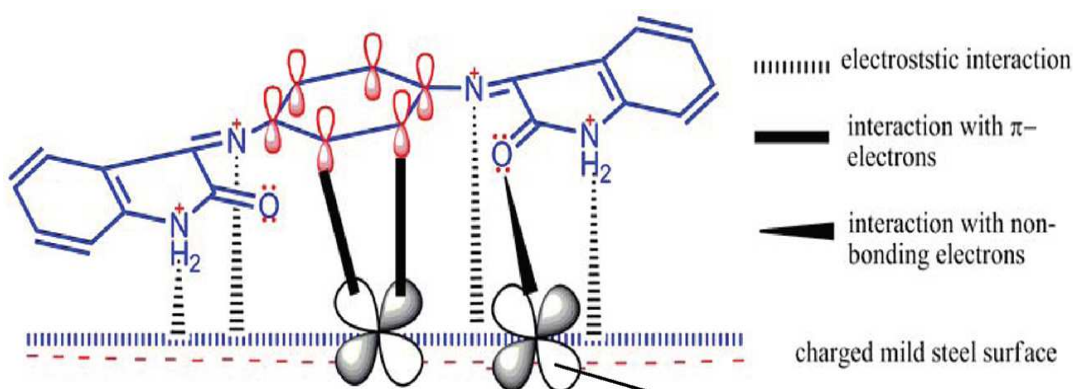


Figure 5. Adsorption of SB of indole onto steel (from ref. 25).

It is well-known that the chloride ions have a small degree of hydration, and due to this, they get first adsorbed on the positively charged steel surface. The adsorption of chloride ions creates an excess negative charge towards the solution side of the metal, and favors a higher adsorption of the PDBI's cationic form. This results in electrostatic interactions between the negatively charged metal surface and the positively charged Schiff base molecule (PDBI⁺), forming a protective (FeCl⁻-PDBI⁺) adsorbed layer. The protonated PDBI molecules are also adsorbed at cathodic sites of mild steel, in competition with hydrogen ions that are reduced to H₂ gas.

Inhibitory action of aminobiphenyl and its Schiff base is studied by Hulya Keles et al. [63]. APh molecule acts as a cathodic inhibitor, whereas APh-S acts as a mixed inhibitor, both obeying Langmuir's adsorption model. APh-S acts as a stronger inhibitor than APh, because of its additional phenylic ring and iminic group. The inhibitor molecule APh-S replaces Cl⁻, because the chelating effect of the Schiff base of APh-S is higher than that of the Cl⁻ ion. Thus, the Cl⁻ ion is removed from the metal surface. Explanation of this mechanism is based on the high chelating effect of the Schiff base of APh-S. In addition to this, there is also the presence of more π -electrons in the additional phenyl rings of APh-S molecule. The π -electrons from the aromatic rings may also interact with the metal surface. Inhibition efficiency of APh-S with respect to APh is due to the π -electrons of the iminic (-C=N) group and the aromatic system and participation of nonbonding electrons present on electronegative donor atoms N and O of the aromatic ring. Aysel Yurt et al. [65] synthesized and studied the effect of novel three Schiff bases, namely, 1,3-bis[2-(2-hydroxy benzylidenamino) phenoxy] propane (P1), 1,3-bis[2-(5-chloro-2-hydroxybenzyl-idenamino) phenoxy] propane (P2), and 1,3-bis[2-(5-bromo-2-hydroxybenzyl-idenamino) phenoxy] propane (P3), on the corrosion of mild steel. Adsorption and thermodynamical studies reveal that the three Schiff bases P1, P2 and P3 undergo chemical adsorption obeying Temkin adsorption characteristics. Chemisorptions of Schiff bases are also proved by quantum mechanical studies, i.e., increase in the inhibition efficiency with decrease of $E_L - E_H$ values, indicating the formation of a coordinate covalent bond. The bond is formed by the sharing or transfer of electrons from N and O atom or π electrons of the aromatic system. From polarization studies, it is noted that P1 acts as mixed inhibitor controlling both metal dissolution, as well as hydrogen evolution, and P2, P3 act as cathodic inhibitors. This is because electronegative atoms, like Cl and Br present in P2, P3, decrease electron density at the N atom of the imine group which is responsible for adsorption. With Cl and Br atoms, an additional negative charge on P2 and P3 destroys the possibility of electrostatic interaction at the anode, and hence, they behave purely as a cathodic inhibitor. The inhibition efficiency follows the order of P1>P3>P2. Rovshan Hasanov et al. [68] have studied the corrosion inhibition effect of two Schiff bases, namely 2-[[4-methoxyphenyl]imino]methyl}phenol-SB1 and 1-[[4-methoxyphenyl] imino]methyl}-2-naphthol-SB2. Both Schiff bases act as mixed corrosion inhibitors, simultaneously controlling both anodic and cathodic processes and obey Langmuir's adsorption model. The adsorption of Schiff base on steel surface

follows HSAB concept of interaction, which is also proved by DFT studies. Here, the steel surface acts as a soft acid, and hence, it prefers to interact with a soft base. According to quantum studies, compounds with a minimum energy difference between HOMO- LUMO may act as a soft base. SB2 possesses a smaller HOMO-LUMO gap than SB1 and, hence, a higher inhibition efficiency. Mechanistically, the adsorption of the inhibitor takes place through permanent dipole sites like $>C=N$, $-O-H$ and $-O-CH_3$ and also with π - electrons of the ring. Since SB2 is bulkier when compared to SB1, its surface coverage is higher than SB1, and hence, it is more efficient. Esmaeel Naderi et al. [64] have studied the effect of SB on the microstructure of steel, i.e., perlite and martensite. Perlite microstructure shows lower corrosion rate than martensite, even in the absence and presence of SB. The efficiency of some pyridine Schiff bases [benzylidene-pyrimidin-2-yl-amine (A), (4-methyl-benzylidene)-pyrimidine-2-yl-amine (B) and (4-chloro-benzylidene)- pyrimidine-2-yl-amine(C)] on corrosion prevention is investigated by H. Ashassi-Sorkhabia et al. [66]. Atoms like O and N of Schiff bases, which have unoccupied orbitals, exhibit an electron accepting tendency. Hence, SB, as an inhibitor, not only donates electrons to unoccupied d orbitals of metals, but it can also accept electrons from metallic orbitals using their anti-bonding orbital to form stable chelates. As a matter of fact, the inhibitor which donates an electron pair to the metal, and receives electrons from the metal, forming a feedback bond, is considered as an excellent inhibitor. The presence of electron donating groups on the Schiff bases structure (such as Cl and CH_3) increases the electron density on the nitrogen of the $C=N$ group, resulting in a high inhibition efficiency. Among the compounds investigated in the present study, the inhibition varies in the order of $C>B>A$, which is also proved by quantum parameters, i.e., C has higher HOMO and lower LUMO energy, as determined by AM1 methods. The inhibitor effect of *N,N*-bis(salicylidene)-2-hydroxy-1,3-propanediamine (LOH) and *N,N*-bis(2-hydroxyacetophenylidene)-2-hydroxy-1,3-propanediamine (LACOH) is studied by Kaan C. Emregül et al. in 2 M HCl [67]. Both compounds have two spaced $-OH$ groups, which intend to form intra molecular hydrogen bonds, leaving only the $-C=N$ group available to link the molecule to the electrode surface, in which case monomolecular adsorption is likely to occur. Steel had an affinity towards N and O bearing ligands. Therefore, the adsorption of these molecules is through the phenolic $-OH$ and $-C=N$ groups. The methyl groups on LACOH tend to increase the electron density on the $-C=N$ group, increasing the bond strength between the molecule and the metal surface, and so, the inhibition efficiency.

Triazoles

Triazoles are termed as some of the most efficient and very often used inhibitors in the pickling process. The compounds inhibit the corrosion process through the adsorption onto the metal surface through the heteroatoms of their ring, and in addition to that, the π electrons of the aromatic system play a vital role in the process of adsorption. F. Bentiss et al. have tested [70] the effect of three of triazole derivatives, namely 3,5-diphenyl-4H-1,2,4-triazole (DHT), 3,5-bis(4-pyridyl)-4H-1,2,4-triazole (4-PHT) and 3,5-bis(4-methylphenyl)-4H-1,2,4-

triazole as inhibitors for steel corrosion in HCl medium. They were shown to reduce the corrosion of steel by forming a stable chemisorbed film controlling both anodic and cathodic corrosion reactions (as revealed by their ΔG values). The adsorption of these compounds on steel obeys Langmuir isotherm, and the inhibition efficiency produced is in the order of 4-MTHT > 4-PHT > DHT. This is because of the replacement of substituents at para position in the phenyl ring of DHT by N-atom in 4-PHT and by $-\text{SCH}_3$ group in case of in 4-MTHT. The same is supported by quantum studies. Additionally, the compound 4-MTHT possesses a higher value of HOMO and a lower value of LUMO energy and a lower dipole moment in comparison with the other two. The four triazole derivatives by Hamdy H. Hassan et al. [69,71], — 5-amino-1,2,4-triazole (5-ATA), 5-amino-3-mercapto-1,2,4- triazole (5-AMT), 5-amino-3-methylthio-1,2,4-triazole (5-AMeTT) or 1-amino-3-methylthio-1,2,4-triazole (1-AMeTT) — , were inhibitors of steel corrosion by adsorbing onto the surface of steel using their N heteroatoms and the substituents. The inhibition efficiency varies in the order of 5AMT>1-AMeTT>5-AMeTT>5-ATA. The high efficiency of 5-AMT is attributed to polarizability of C=S group in the molecule. Shengtao Zhang et al. have investigated [72] the relationship between molecular structure and their inhibition effect of two triazole derivatives, namely, 1-[2-(4-nitro-phenyl)-5-[1,2,4]triazol-1-ylmethyl-[1,3,4]oxadiazol-3-yl]-ethanone (NTOE) and 1-(4-methoxy-phenyl)-2-(5-[1,2,4]triazol-1-ylmethyl-4H-[1,2,4]triazol-3-ylsulfanyl)-ethanone (MTTE) on steel corrosion in HCl media. Quantum chemical calculations were performed using Ab initio method. Triazole derivative molecules interact with the steel surface on the basis of donor-acceptor interactions between the π -electrons of the benzene ring, $-\text{C}=\text{N}-$ and the vacant d-orbitals of iron atoms. The three triazole derivatives namely, triazole, aminotriazole and benzotriazole, were tested as inhibitors by K.F. Khaled [74]. The adsorption of these inhibitors on the mild steel obeys Langmuir's adsorption isotherm. Among the three tested triazoles, amino triazole has served as the best inhibitor, which is also proven by molecular modeling (a quantum technique). It is determined that the charge density distribution on aminotriazole is more intense than on triazole and benzotriazole. This fact explains that the adsorptive power of aminotriazole is stronger (because it binds more strongly on iron surface) than that of triazole and benzotriazole. This is also confirmed by the values of HOMO and LUMO energies and the value of dipole moment. Aminotriazole has got a higher value of HOMO and a lower value of LUMO and dipole moment, which is the essentials of a good inhibitor. Weihua Li et al. have investigated [73] the effect of three synthesized triazole derivatives, namely (4-chloro-acetophenone-O-1-(1,3,4-triazolyl) metheneoxime (CATM), 4-methoxyl-acetophenone-O-1-(1,3,4-triazolyl)-metheneoxime (MATM) and 4-fluoro-acetophenone-O-1-(1,3,4-triazolyl)-metheneoxime (FATM), which were proven as efficient inhibitors for steel corrosion in acidic media. The adsorption of these triazoles obeys Langmuir isotherm law, and the inhibition efficiency follows the order CATM>MATM \approx FATM. The inhibition efficiency depends upon the substituents Cl, $-\text{OCH}_3$ and F^- at 4th position. The quantum parameters, HOMO and LUMO electronic distributions, showed the formation of donor –acceptor

interaction between steel and inhibitors. This interaction occurs by utilizing π -electrons and $-C=N-$ in all three compounds.

Miscellaneous compounds

Jun Zhao et al. have studied [75-76] the effect of aqueous extract of ciggeratebuts(Cb) as a corrosion inhibitor for mild steel. The aqueous solution of Cb contains aromatic amides, nicotine and its compounds. Weight loss and electrochemical studies reveal that Cb acts as a mixed inhibitor, controlling both anodic dissolution and cathodic hydrogen evolution. As aging proceeds, the solution of Cb produces higher efficiency. Its inhibition action is via the adsorption onto the metal surface. The adsorption of the inhibitor could occur due to the formation of an oxidation film, i.e., oxidants of inhibitor form insoluble salt on interaction with iron. This is because the aerobic solution oxides the existing compounds. The inhibition effect is proved by electrochemical noise (EN) studies. It is defined as the ratio of standard deviation of potential noise, σ_E , to coupling current fluctuations σ_I i.e., $R_n = \sigma_E / \sigma_I$. Resistance of noise follows the order of blank < anaerobic < aerobic. This is inversely related to the corrosion rate, i.e., blank > anaerobic > aerobic. |

N.O. Obi-Egbedi et al. have synthesized [77] and studied inhibition of phenanthroline derivative, 2-(6-methylpyridin-2-yl)-1H-imidazo[4,5-f][1,10] phenanthroline(MIP). The inhibitory effect is caused by the adsorption of MIP on the mild steel surface, which limits the hydrogen evolution by blocking its cathodic sites on steel with electrostatic interaction of protonated MIP through a SO_4^{2-} bridge. In MIP, the presence of imidazole and phenanthroline rings, with several π -electrons and aromatic systems containing five N atoms, can induce greater adsorption of the molecule. The formation of donor-acceptor surface complexes occurs between protonated MIP and the steel surface through electrostatic interaction with the sulphate bridge. Electrostatic interaction also takes place by partial transference of electrons from the N atoms and the delocalized π -electrons around the heterocyclic rings of MIP to the metal surface. The physisorption of MIP is also proved by UV- studies and free energy calculation.

Formazan of benzaldehyde (FB) is investigated as a corrosion inhibitor by B. Anand for mild steel in HCl media [78]. Electrochemical studies have revealed it acts as a mixed inhibitor, simultaneously controlling both anodic and cathodic corrosion processes. A free energy value reveals that FB undergoes physical adsorption. In observing the structure of the compound we may notice that it contains a great number of N-H bonds which get protonated in acidic media. This protonated FB may adsorb onto steel through the Cl bridge.

E. Machnikova et al. have studied [79] the effect of three furan derivatives, 2-methyl furan, furfuryl alcohol and furfuryl amine, as corrosion inhibitors for mild steel. Electrochemical studies of the inhibitor suggest that all three molecules act as a mixed inhibitor, controlling both anodic and cathodic processes. The inhibitor molecules undergo chemisorption and form a layer over the surface of metal, by forming a bond between empty d-orbitals of metal with lone pair electrons or π -electrons of the inhibitor, which is proved by the decrease in

capacitance of the electrical double layer. There is a further inhibition efficiency of furfuryl alcohol > furfuryl amine > 2-methyl furan. This is because furfuryl alcohol polymerizes on steel, thereby preventing it from corrosion, and furfuryl amine contains one additional heteroatom in relation to 2-methyl furan; hence, its inhibition is higher than 2-methyl furan, which is proved by molecular modeling and quantum calculations.

Gao Jiancun et al. have studied [80] the corrosion inhibition effect of α,β -unsaturated compounds, namely, cinnamaldehyde, benzalacetone and chalcone. They have studied the IR spectra of the compound before and after the corrosion process, w.r.t, the polymerization process of the three compounds. Cinnamaldehyde polymerizes completely, by forming a thin oil film on the steel surface, as the disappearance of functional groups $-C=C-$, $-C=O$ takes place, and corresponding peaks are observed after inhibition. Benzalacetone undergoes partial polymerization on steel; slight changes in characteristic peak of groups $-C=C-$, $-C=O$ can be seen. In the case of chalcone, there are no changes in the IR spectra, so, no polymerization of compound is seen. All the three behave as mixed inhibitors, with an increase in concentration and temperature; cinnamaldehyde and benzalacetone act as anodic inhibitors. In spite of good polymerizing properties, cinnamaldehyde has poor inhibition efficiency, as its inhibition effect only occurs by the π -electrons of the aromatic ring. In benzalacetone, both $-C=O$, π -electrons of the aromatic ring are involved, and in chalcone the inhibition efficiency is high, since it possesses two aromatic rings with $-C=O$ group.

A. Jamal Abdul Nasser et al. have used [81] N-[morpholin-4-yl(phenyl)methyl]acetamide(MPA) as a cathodic inhibitor for steel. It shows 91% inhibition efficiency in weight loss measurement. The adsorption of MPA on steel surface obeys Langmuir isotherm. MPA structurally possesses N and O donor atoms of the morpholine ring. In addition, these heteroatoms, amide linkage, one phenyl ring, all these greatly influence the adsorption and film forming tendency of MPA. The reaction site in MPA is a lone pair of electrons on hetero atoms and π - electrons of the aromatic ring. MPA acts as a Mannich base and gets protonated in an acidic solution. There are two different mechanisms of action. In the case of neutralized MPA molecule, chemisorptions occur, by the interaction of vacant d-sites of steel with the heteroatom and p- π electrons of the aromatic ring of MPA. M. Lebrini et al. investigated [82] the corrosion inhibitive effect of two thiadiazole compounds. The two thiadiazole compounds, 2,5-bis(2-thienyl)-1,3,4-thiadiazole (2-TTH) and 2,5-bis(3-thienyl)-1,3,4-thiadiazole (3-TTH), were studied as corrosion inhibitors for mild steel [86]. The compounds act as mixed type inhibitors obeying Langmuir isotherm. 3-TTH has shown higher efficiency than 2-TTH, as revealed by the results of chemical, electrochemical and Quantum DFT studies. From XPS analysis, it is clearly stated that the compounds get chemisorbed to the steel surface using their N and S atoms, forming a stable film. There is a shift in the peaks corresponding to $=N-$ and $-S-$ towards lower binding energy, indicating the formation of a stable film on steel, and the same is supported by the thermodynamic calculation.

R. Tripathi et al. have studied [83] the inhibitive effect of four derivatives of thiourea, namely: 1-(2,6-diazene)-3-benzyl thiourea (ST1), 1-(3'-pyridyl) - 3 - benzyl thiourea (ST2), 1 - (3'- pyridyl) - 1 -phenyl thiourea (ST3) and 1-(2'-pyridyl)-3-phenyl thiourea (ST4). They prevent the corrosion of steel in acidic media, forming a chemisorbed film which acts as a barrier between steel and corrosive media. The adsorption of the compounds obeys Langmuir isotherm, and inhibition efficiency varies accordingly, as follows: ST1>ST2>ST3>ST4. These STs interact with steel surface using their N and S atoms and π - electrons of both pyridyl and benzene system, forming a compact barrier film between steel and corrosive media. Among the four STs, ST1 shows the highest corrosion inhibition, since the availability of electrons on nitrogen atoms of thiourea and on pyrimidine ring to donate to the Fe is higher than that of ST2. But in the case of ST3 and ST4, the lone pair of electrons on N of thiourea moiety is not available for adsorption, since it directly attaches to the phenyl ring, generating the inhibition trend.

Ying Yana et al. have investigated the effect of the purines and their derivatives [84], viz., guanine, adenine, 2,6-diaminopurine, 6-thioguanine and 2,6-dithiopurine as inhibitors for steel corrosion. The inhibition efficiency of the compounds follows the order: 2,6-dithiopurine > 6-thioguanine > 2,6-diaminopurine > adenine > guanine. All the compounds act as mixed inhibitors controlling both anodic and cathodic corrosion reactions. The adsorption of these compounds occurs by utilizing entire purine moiety, and the adsorption may take place in three ways. The first is as a neutral molecule that, by sharing an electron pair between electronegative atoms and mild steel, gets directly adsorbed to steel via chemisorption mechanism. The second is through back bonding, i.e., purines accept the electron from metal surface, while the final one is through two heterocyclic rings, which occurs by hyper conjugation.

A newly synthesized amino acid ionic liquid, 1-octyl-3-methylimidazolium L-prolinate ([Omim]Lpro), was investigated as an inhibitor for mild steel in 0.5 M H₂SO₄ solution by X. Zheng et al. [87]. The obtained results have revealed that [Omim]Lpro was a mixed-type inhibitor with a predominantly cathodic action for mild steel in 0.5 M H₂SO₄ solution, and the adsorption of [Omim]Lpro on the mild steel surface was found to obey the El-Awady thermodynamic-kinetic model and Flory-Huggins isotherm. According to the results obtained from the experiments and theoretical analysis, 1-octyl-3-methylimidazolium L-prolinate ([Omim]Lpro) mainly undergoes physical adsorption on the mild steel surface, and, to some extent, chemical adsorption. In acidic solutions, [Omim]Lpro exists predominantly as protonated species (Omim cation and Lpro cation); these cations may directly adsorb onto the cathodic sites of the mild steel surface and decrease the evolution of hydrogen. On the other hand, the adsorption on anodic sites probably occurs through the π -electrons of the imidazole ring and the free lone-pair electrons of nitrogen and oxygen heteroatoms, which decreases the anodic dissolution of mild steel. However, due to the weak electron-donating ability of cations, the tendency to chemical adsorption is very weak. In addition, it can be presumed that, when the concentration of [Omim]Lpro is lower (0.5-5 mM), Omim cation and Lpro cation show a synergistic effect, but when the

concentration of [Omim]Lpro is higher (10 mM), there is a competition between Omim cation and Lpro cation in terms of adsorption at cathodic site, thus exhibiting an antagonistic effect.

C. Verma et al. [88] synthesized and studied the effect of three 3-amino alkylated indoles (AAIs), namely, N-((1H-indol-3-yl)(phenyl)methyl)-N-ethyl ethanamine (AAI-1), 3-(phenyl(pyrrolidin-1-yl)methyl)-1H-indole (AAI-2) and 3-(phenyl(piperidin-1-yl)methyl)-1H-indole (AAI-3) on mild steel corrosion in 1 M HCl solution. All three compounds act as good inhibitors for mild steel, exhibiting the efficiency of 94.34% for AAI-1, 96.08% for AAI-2 and 96.95% for AAI-3. All the compounds are cathodic type inhibitors, and adsorption of these compounds on steel obeys Langmuir adsorption isotherm equation. Quantum studies together with MD simulation process describe the mode of adsorption of these molecules on steel. During the MD simulation process, AAIs moved gradually near the Fe (110) surface with an almost flat orientation. Therefore, it can be concluded that investigated inhibitors utilize their planar phenyl and indole rings moieties to adsorb onto the mild steel surface. Further, using the nonbonding electrons of the N atoms and π -electrons of the indole and phenyl moieties, AAIs form back bonding with the empty d-orbitals of the steel surface (Fe atoms). Generally, the energy is released when the inhibitor is adsorbed on the steel substrate. The values of the interaction energy ($E_{\text{interaction}}$) and binding energy (E_{binding}) between studied inhibitors and Fe (110) surface are determined when systems reach equilibrium. The negative value of ($E_{\text{interaction}}$) of all AAIs suggests spontaneous adsorption of these compounds on Fe (110) surface. The value of the binding energies (E_{binding}) of studied inhibitors follows the order: AAI-3 > AAI-2 > AAI-1, which is in accordance with the order of their inhibition efficiencies obtained experimentally.

Conclusions

In spite of much advances in the field of corrosion studies, it is not possible to predict a single generalized mechanism of action for inhibitors in acidic media. It can be generalized that the inhibitor undergoes adsorption at the metal surface, which prevents the interaction of the latter with the corrosive acid media. Further, the nature of metal, media and physico-chemical, electronic and structural properties of the chosen inhibitor have also played a prominent role, while explaining the mechanism. From this study it is inferred that organic compounds with S, N and O-heteroatom in their structure and phyto-chemicals of green inhibitors are the most efficient inhibitors, and surfactants are efficient inhibitors within their CMC concentration. In this respect an attempt is made here to summarize the possible types of inhibition process mechanisms for different classes of inhibitors.

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