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Chapter

Organic Corrosion Inhibitors

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Abstract

Organic corrosion inhibitors are preferred due to its environmental friendly and effectiveness at a wide range of temperatures. The efficiency of an organic inhibitor depends on the size of the organic molecule, aromaticity, type, and number of bonding atoms or groups in the molecule (either π or σ), nature and surface charge, the distribution of charge in the molecule, and type of aggressive media. The presence of polar functional groups with S, O, or N atoms in the molecule, heterocyclic compounds and pi electrons present in the molecule also increases the efficiency of these organic corrosion inhibitors. The use of computational chemistry such as density functional theory (DFT), molecular dynamic simulation (MD), Monte Carlo (MC) simulations, and quantitative structure-activity relationship (QSAR) modeling has been applied for study of corrosion inhibition properties of organic compounds. This chapter will explain about theoretical and computational study of organic compounds as corrosion inhibitors.

Keywords: organic corrosion inhibitors, physisorption, cathodic inhibitors, anodic inhibitors, mixed inhibitors

1. Introduction

Corrosion is a natural process and also a universal phenomenon of metals. Corrosion is the deterioration of the metal in the presence of the surrounding environment by chemical or electrochemical means [1–10]. The corrosion of metals results into a huge loss of economy in the world [11–14]. There are various methods to reduce or prevent corrosion. The use of corrosion inhibitors is one of the ways to protect metal surfaces against corrosion [15–18]. In the early days, inorganic compounds such as nitrates, chromates, borates, silicates, chromates, phosphate, and molybdates were used as inhibitors for the prevention of corrosion [19–31]. Due to the toxic and environmental effects of that inorganic inhibitor, scientists start using environment friendly organic inhibitor for prevention of corrosion [32–35]. The organic compounds that contain mainly nitrogen, oxygen, sulfur phosphorus, and multiple bonds or aromatic rings in their structures act as corrosion inhibitors [36, 37]. Various heterocyclic aromatic compounds are studied as organic inhibitors [38–48]. It has been studied by various groups that carboxylate and amine of aliphatic compounds can be used as organic inhibitors [49–52].

In this article, there will be a detailed study of organic compounds as inhibitors and their computational and theoretical studies will be explained. There are various reviews papers on molecular modeling of compounds as corrosion inhibitors by
various groups. The DFT and MD simulation studies about adsorption of the organic corrosion inhibitors and the metal surface in various corrosive environments.

2. Organic corrosion inhibitors

Organic corrosion inhibitors are preferred due to its environmental friendly and effectiveness at wide range of temperatures [53–59]. The efficiency of an organic inhibitor depends on the size of the organic molecule, aromaticity, type, and number of bonding atoms or groups in the molecule (either \(\pi\) or \(\sigma\)), nature and surface charge, the distribution of charge in the molecule and type of aggressive media. The presence of polar functional groups with S, O, or N atoms in the molecule, heterocyclic compounds and \(\pi\) electrons present in the molecule also increases the efficiency of these organic corrosion inhibitors. The adsorption of the molecule on the metal surface depends on the polar function of the molecule. The organic compound that contains oxygen, nitrogen and/or sulfur blocked the active corrosion sites by adsorbing on the metallic surface.

The organic compounds act as cathodic, anodic, and mixed inhibitors. The organic molecules exhibiting a strong affinity for metal surfaces show good inhibition efficiency. The organic compounds adsorb on the surface of the metal to form a protective film which displace water from the metal surface and protect it against corrosion. The organic inhibitors adsorb onto the metallic surface depend on the chemical structure of the inhibitors, type of environment, and surface charge of the metal. The inhibitor adsorption on metal surfaces occurs through donor-acceptor interactions (physical, chemical, or mixed type) [60–63]. The organic inhibitors are adsorbed on metal surface either by physisorption or chemisorptions mechanism. The physisorption occurs through an electrostatic interaction between the metal surface and inhibitor's charged molecule [64–66]. The chemisorptions mechanism occurs through charge transfer share between the adsorbed inhibitor molecules and the metal surface.

The mechanism of organic corrosion inhibition takes place in two steps. The first step involves the transfer of the corrosion inhibitors over the metallic surface. In the second step interactions between metal surface and adsorbed inhibitor molecules occur [67–69]. In physisorption, the adsorbed inhibitor molecules are not in direct contact with the metallic surface. A layer of solvents which are already adsorbing on the surface molecules separated the inhibitor molecules [70, 71].

The mechanism of organic corrosion inhibition in aqueous medium can be occurs as follows [72].

\[
\begin{align*}
M + nH_2O & \leftrightarrow M(H_2O)_{n\text{ads}} \quad (1) \\
M(H_2O)_{n\text{ads}} + 2X^- & \leftrightarrow M[(H_2O)_n(X)_2^-]_{\text{ads}} \quad (2) \\
M[(H_2O)_n(X)_2^-]_{\text{ads}} & \leftrightarrow M[(H_2O)_n(X)_2]_{\text{ads}} + 2e^- \quad (3) \\
M[(H_2O)_n(X)_2]_{\text{ads}} & \leftrightarrow M^{2+} + OH^- + 2X^- + H^+ \quad (4)
\end{align*}
\]

In the presence of organic corrosion inhibitor (INH), the following mechanism operates [73, 74].

\[
M + nH_2O \leftrightarrow M(H_2O)_{n\text{ads}} \quad (5)
\]
The effect of organic compounds as corrosion inhibitors and adsorption on metal surfaces depends on various factors. Temperature is one of the factors. The increase in temperature results in a decrease in the inhibition of corrosion due to adsorption on metallic surface decreases [75, 76]. Then inhibitor concentration is another parameter for the effectiveness of the organic inhibitor molecules. With increasing inhibitor concentration, inhibition efficiency of compounds increases. However, after certain concentration, there is no further enhancement of inhibition. The effectiveness of the organic inhibitor also depends on the electronic structure and molecular size of the molecule [77, 78]. The organic compound with high molecular size generally shows a better corrosion inhibitor than compound with lower molecular size. But, too big molecular size compound show a decrease in adsorption on metallic surfaces due to a decrease in solubility. The molecular electronic structure is one of the aspects of corrosion inhibitors. The planar geometry organic compound acts as better corrosion inhibitor than with vertical geometry of the compounds. The aromatic organic compounds having conjugation in the form behave as effective corrosion inhibitors. The aromatic compound containing electron-donating substituent such as –OCH₃, –CH₃, –OH, –NH₂, –NHR, and –NR₂ increases the organic corrosion inhibitor molecules, whereas, electron-withdrawing substituent such as –CN, –COOH, –COOC₂H₅, and –NO₂ decreases inhibitor molecules [79]. The effect of aromatic substituted substituent on corrosion inhibition can be determined by Hammett substituent constant (σ) values. The corrosion inhibition efficiency of substituted aliphatic linear and cyclic compounds can be determined by Taft constant (σ*) values [80]. The Hammett equation is shown below

\[
\log \left(\frac{K_R}{K_H}\right) = \rho \sigma
\]

whereas \(K_H\) and \(K_R\) are equilibrium constants for non-substituted and substituted compounds. \(\sigma\) is the Hammett constant, \(\rho\) is its magnitude depending on the nature of metal-inhibitor interactions.

3. Computational method used for corrosion inhibitors

There are various experimental methods for the evaluation of the inhibition performance of corrosion inhibitors. The synthesis of organic compounds for corrosion inhibitors using experimental methods is expensive and time-consuming. The synthesis of organic inhibitors requires multiple steps and also so many side products are generated in the synthesis of organic molecules. Recently, computational methods have been used extensively for the study of corrosion inhibition [81–95]. The corrosion inhibition can be known by knowing the mechanism of interaction between the inhibitor molecules and the metal surface. The interaction of the metal and inhibitor at the atomic and molecular levels cannot be understood by experimental study. The deeper insights into the mechanism of corrosion inhibitors on metal surfaces can be understood by molecular modeling method [96]. Molecular modeling techniques provide mechanistic processes at the atomic and molecular levels [97–118].
The behaviors of atomic and molecular interactions at microscopic and macroscopic can be analyzed by molecular modeling techniques [119, 120]. The interactions between molecules at the microscopic level can be known by molecular modeling simulations. Molecular modeling techniques are divided into three categories: ab initio electronic structure methods, semi-empirical methods, and atomistic simulation.

The ab initio method is also called first principles electronic structure method and is based on the law of quantum mechanics. The different ab initio methods are the Hartree–Fock Self-Consistent Field (HF-SCF) method, Møller–Plesset perturbation theory (MPn), coupled cluster (CC), and density functional theory (DFT). The density functional theory (DFT) has been used widely for understanding metal-inhibitor interactions at the molecular level.

3.1 Density functional theory

DFT has been used for understanding the molecular structural behavior of corrosion inhibitors [121–125]. In the DFT method, one function is determined in terms of another function, which is essentially the meaning of the word “functional”. The energy of a system in the DFT method is obtained from its electron density. Commonly used DFT methods are the B3LYP, BLYP, B3P86, B3PW91, and PW91. Basis sets are sets of linear combinations of mathematical functions that are used to describe the shapes of atomic orbitals. The use of basis sets is necessary to be able to carry out ab initio calculations. Basis sets describe atomic orbitals by assigning a group of basis functions to each atom within a molecule. There exist broad lists basis sets that are used to perform ab initio calculations. The DFT/B3LYP method using the 6-31G and 6-311G basis sets is the most widely used in corrosion inhibition studies.

The mechanism of corrosion inhibition can be understood by using DFT simulations. DFT simulation helps in finding the interactions of inhibitor with metal surface. For understanding the interactions of inhibitor with metal surface, the computational methods provide information about highest occupied (HO) and lowest unoccupied (LU) molecular orbitals (MO), frontier orbital energies, energy band gap, hardness, electronegativity, Mulliken and Fukui population analyses, electron-donating power, electron-accepting power, chemical potential, hardness, softness, dipole moment, and number of electrons transferred.

3.1.1 HOMO and LUMO

The adsorption ability and corrosion inhibition effectiveness of a compound can be linked to energy of frontier molecular orbital (FMOs; $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$), hardness (Z), electronegativity (w), dipole moment (m), softness (s), and fraction of electron transfer (DN). The chemical relativities of molecules in a corrosion inhibitor molecule are related to HOMO and LUMO electron densities. The highest occupied molecular orbital (HOMO) donates electrons to the free d orbital of a metal. The lowest unoccupied molecular orbital (LUMO) accepts electrons from the metal. Lower values indicate higher tendency of accepting electrons. The positive values are connected with chemisorptions, whereas negative values are with physisorption. The higher electron-donating capability is associated with a higher HOMO in the heteroatom molecules heteroatom.

HOMO and LUMO were associated with electron-donating and electron-accepting abilities of molecules, respectively, according to FMOs theory. Inhibitor molecules having high energy of HOMO will be effective to transfer the electrons to a metallic
surface and low LUMO energy value shows that the molecule is a good electron acceptor. Koopmans theorem [126] is a bridge between DFT and MO theory and it can be used in the prediction of ionization potential (IP) and electron affinity (EA) values of molecules. According to this theorem, IP and EA can be expressed via the following equations:

\[
IP = -E_{\text{HOMO}} \tag{9}
\]

\[
EA = -E_{\text{LUMO}} \tag{10}
\]

Further, the energy difference between LUMO and HOMO called an energy gap (ΔE) is also an essential parameter toward the description of reactivity of a molecule.

\[
\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}} \tag{11}
\]

ΔE having a large value show low reactivity of molecules with metal surface while a molecule with a low value of ΔE strongly adsorbed on a metal surface.

3.1.2 Electronegativity (\(\eta\)), chemical potential (\(\mu\)), hardness (\(\eta\)), and softness (\(\sigma\)) indices

The \(\eta\), \(\mu\), \(\eta\), and \(\sigma\) parameters are related to the total electronic energy (E) with respect to the number of electrons (N) at a constant external potential. The \(\eta\) is defined as the negative value of \(\mu\). Within the framework of finite differences approaches, these parameters can be expressed in the form of ground-state IP and ground-state EA values of a chemical compound. The theoretical formulas can be expressed as [127]:

\[
\mu = -\frac{IP + EA}{2} \tag{12}
\]

\[
\eta = -\frac{IP - EA}{2} \tag{13}
\]

\[
\sigma = -\frac{1}{\eta} \tag{14}
\]

The electron-donating power and electron-accepting power of the molecule to accept and donate electrons are related to IP and EA. The inhibition abilities of the molecule based on their ability to accept and receive electrons provide information.

3.1.3 The fraction of electrons transferred (\(\Delta N\))

The tendency of an inhibitor molecule to transfer its electron to a metal surface, the hardness, and electronegativity predict \(\Delta N\). The interaction between the metal surface and inhibitor molecule on the basis of the fraction of electrons transferred. An inhibitor can transfer its electron if \(\Delta N > 0\) and vice versa if \(\Delta N\) [128–130].

3.1.4 Fukui indices (FIs)

The local reactivity and selectivity of molecule can be understood by Fukui functions. The nucleophilic and electrophilic regions of attack of inhibitor molecules are
provided by Fukui function. The Fukui Indices (FIs) pinpoint the reactive sites in which the electrophilic or nucleophilic attacks are large or small. HSAB theory gave the prediction and interpretation of many CQ parameters and Fukui functions is also an early attempt in this direction. Fukui Indices \( f(r) \) is the first derivative of \( \rho(r) \) with respect to the number of electrons \( (N) \) at a constant external potential \( v(r) \). FIs were identified with respect to hard or soft reagents by involving the HSAB principle. A simple approximation can be used with the aid of finite difference approximation and Mulliken’s population analysis in which FIs were determined [131].

### 3.2 Atomistic simulations

Atomistic simulations also called force field methods or molecular mechanics are based on the principles of classical physics. The atomistic simulations are the investigation and simulation of physical phenomena on a molecular level. The two well-known atomistic simulation methods are the molecular dynamics (MD) [132–135] and Monte Carlo (MC) [136, 137] simulation techniques.

#### 3.2.1 Molecular dynamics (MD) simulations

MD simulations provide the actual trajectory of a system by simulating the time evolution of the system. The concept of MD simulation is based on solving Newton’s equations of motion for the atoms in the simulation system using numerical integration [138, 139].

##### 3.2.1.1 Total energy minimization

The first step in atomistic simulations is to find a stable structure by the total energy minimization process (geometry optimization). The lowest energy configuration of the atoms in a system can reach by adjusting their coordinates. The net forces acting on the atoms are zero.

##### 3.2.1.2 Ensemble

An ensemble is defined by its thermodynamic states such as constant pressure, temperature, and volume mimicking experimental conditions during a molecular mechanics simulation. The main ensembles used for the molecular dynamics simulation are the microcanonical ensemble (NVE), canonical ensemble, isobaric-isothermal (NPT), and grand canonical ensembles (\( \mu VT \)) [140].

##### 3.2.1.3 Force fields

The set of parameters acting on the nuclei of atoms by which the potential energy (U) of a system is calculated of a molecular system is called force fields. To find a correct force field is a challenging task in every simulation for a given system. Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) is the general force fields used for corrosion inhibition studies. In addition to ab initio calculations, COMPASS was parameterized considering various experimental data including organic compounds made with H, C, N, O, S, and P atoms, halogens, and metals. Universal force field (UFF) [141, 142], is an all-atom
potential containing parameters for each atom, and the consistent-valence force field (CVFF) is a generalized valence force field that allows treating organic molecules as well as metals [143–145].

3.2.1.4 Periodic boundary condition

Atomistic simulations are usually carried out in a simulation box. It can be obtained by treating a small system of about 100–10,000 particles using the periodic boundary condition approach. The corrosion inhibition systems are infinite systems where thousands of atoms and molecules are involved. The periodic boundary condition eliminates surface effects caused by the finite size of a system, and makes it more of an infinite one. In periodic boundary conditions, all atoms in the simulation box are replicated throughout space to form an infinite lattice.

3.2.2 Monte Carlo (MC) simulations

The MC method can simulate a system under thermodynamic equilibrium [146]. MC has the advantage of probabilistic investigation of the equilibrium behavior of systems as a function of temperature (Metropolis Monte Carlo) and advances the state of reactive systems through time (Kinetic Monte Carlo) [147]. The Metropolis MC, kinetic Monte Carlo (kMC), and quantum Monte Carlo are used in many physical and chemical applications based on the concept of Monte Carlo. Metropolis MC is simple and mostly used to study the interaction between inhibitor molecules and surface of metals in corrosion inhibition.

3.2.2.1 Interaction and binding energies

The interaction energy is defined as the required energy for one mole of an inhibitor molecule to be adsorbed on a metal surface [148]. For a simulated system in a vacuum, it can be determined using the following equation [149, 150]:

\[ E_{\text{inter}} = \frac{E_{\text{Total}}}{C_0} - (E_{\text{Surface}} + E_{\text{inh}}) \]  

In the presence of a solvent:

\[ E_{\text{inter}} = \frac{E_{\text{Total}}}{C_0} - (E_{\text{Surface + solution}} + E_{\text{inh}}) \]  

where \( E_{\text{Total}} \), \( E_{\text{Surface}} \), \( E_{\text{Surface + solution}} \), and \( E_{\text{inh}} \) denote the total energy of the simulated system, surface without solution, surface with solution, and inhibitor molecule alone, respectively.

The binding energy is defined as the negative values of the interaction energy. A large binding energy implies that the inhibitor molecule can be strongly adsorbed over a metal surface [151, 152].

\[ E_{\text{binding}} = -E_{\text{inter}} \]  

A representative case where interaction and binding energies are used to discuss the adsorption behavior of corrosion inhibitors has been performed by Lgaz et al. [153].
4. Aliphatic compounds as an organic corrosion inhibitor

Jia-jun Fu et al. carried out experimental, MD simulations and DFT calculations to investigate the corrosion inhibition properties of four amino acid compounds namely L-cysteine, L-histidine, L-tryptophan, and L-serine amino acid for mild steel in hydrochloric acid solution [154]. The optimization of the amino acid compounds has been performed using B3LYP Density Functional Theory (DFT) with 6-311G (d,p) basis set with the Gaussian 03 W program. This basis set will provide $E_{\text{HOMO}}$, $E_{\text{LUMO}}$, $\Delta E$, and $\mu$. The Fukui function calculations were performed with DMol3 version 4.3 available in Material Studio software (Accelrys, San Diego, CA), using a PBE (Perdew, Burke, and Enzerhof) functional and a double-numeric quality basis set with polarization functions (DND). Dmol3 uses a Mulliken population analysis.

The optimized structures of the four amino acid compounds were shown in Figure 1. Additionally, the orbital density distributions of $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ for amino acid compounds were shown in Figure 2. From this DFT calculation of these four amino acids, the $E_{\text{HOMO}}$, $\Delta E$ and $\Delta N$ provide that the order of the inhibition efficiency of these inhibitors follows the sequence: L-Try > L-His > L-Cys > L-Ser.

Mohammed et al. [155] carried out a study of the inhibition of iron corrosion in HCl solutions by three amino acids, namely alanine (Ala), cysteine (Cys), and S-methyl cysteine (S-MCys). The effectiveness of amino acids, alanine (Ala), cysteine (Cys), and S-methyl cysteine (S-MCys) as safe corrosion inhibitors for iron in aerated stagnant 1.0 M HCl solutions have been evaluated by Tafel polarization and

![Figure 1. Optimized structures of four amino acid compounds.](image1)

![Figure 2. The frontier molecular orbital distribution of four amino acids compounds.](image2)
impedance measurements. They have also performed molecular dynamics (MD) and density functional theory (DFT) for their inhibition efficiency. The electronic density distribution of HOMO (the highest occupied molecular orbital) and LUMO (the lowest unoccupied molecular orbital) for the studied amino acids were shown in Figure 3. From these studies, Cys has the lowest $E_{\text{HOMO}}$ and the highest $E_{\text{LUMO}}$ then S-MCys and Ala. The experimental data and computational study has been in agreement that Cys has a higher inhibition efficiency than alanine (Ala) and S-methyl cysteine (S-MCys).

Obot et al. studied the mechanism of 2-mercaptobenzimidazole adsorption on Fe (110), Cu (111), and Al (111) surfaces by applying DFT and molecular dynamics simulations [156]. The DFT study was performed using B3LYP, 6-31G (d,p) basis set in the gas phase. The inhibition was performed by MD simulations, optimization using the COMPASS force field under the NVT ensemble and PBC at a simulation time of 50 ps. The mechanism of corrosion inhibition of 2-mercaptobenzimidazole (2-MBI) on Fe, Cu, and Al surfaces Density functional theory (DFT) and molecular dynamics (MD) simulations.

Canul and Rosado studied the Inhibition Effect of Sodium Glutarate toward Carbon Steel Corrosion in Neutral Aqueous Solutions [157]. They investigated the Inhibition Effect of Sodium Glutarate in a near-neutral 0.02 M NaCl solution at ambient temperature for a range of concentrations (1–100 mM) by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements. Sodium glutarate showed a poor inhibitive action for corrosion of carbon steel in a 0.02 M NaCl solution when used in concentrations of 1 mM and 5 mM. However, open circuit potential and polarization curve measurements give evidence that full chemical passivation is accomplished for concentrations of 32 mM or higher; a significant improvement in protective is achieved. Investigation of the effect of temperature showed that increasing the temperature from 22 to 55°C decreases the inhibition efficiency from 96 to 89%, indicating good stability of the protective film in this temperature range.

Ambat and co-workers reported electrochemical and molecular modeling studies of CO$_2$ corrosion inhibition characteristics of alkanolamine molecules (ethanolamine, diethanolamine, and triethanolamine) for the protection of 1Cr steel [158]. The DFT
calculations were performed with the Quantum Espresso package on a Fe (110) surface and a FeCO$_3$ (104) surface. The experimental results and molecular modeling calculations using DFT found that the inhibitor efficiency for the ethanolamine on Fe(110), FeCO$_3$(104), and Fe$_3$C(001) was the highest.

Obot and co-workers performed density functional theory and molecular dynamics simulation for study the corrosion inhibition for three amine derivatives, namely, N1-(2-aminoethyl)ethane-1,2-diamine (DETA), N1-(2-(2-aminoethylamino)ethyl)ethane-1,2-diamine (TETA) and N1-(2-(2-(2-aminoethylamino)ethylamino)ethylamino)ethylamine-1,2-diamine (PEHA) on the steel surface [159]. They have calculated $E_{\text{HOMO}}$, $E_{\text{LUMO}}$, energy gap ($\Delta E$), electron affinity ($\chi$), global hardness ($\eta$), softness ($\sigma$), and the fraction of electron transferred ($\Delta N$) from the inhibitor molecule to the metal surface. The quantum chemical parameters $E_{\text{HOMO}}$, $E_{\text{LUMO}}$, $\Delta E$, hardness ($\eta$), softness ($\sigma$), and fraction of electron transferred ($\Delta N$) are in good agreement with the experimental findings. The nucleophilic and electrophilic characteristic of inhibitor molecules were analyzed from Fukui indices. MD simulation performed by COMPASS force field. The interaction energies at 298 K temperature are $-355.30$, $-455.93$, and $-784.74$ kJ/mol for DETA, TETA, and PEHA, respectively, on the Fe (1 1 0) surface. PEHA has maximum interaction energy value and possesses better inhibition effectiveness than DETA and TETA. The corrosion inhibition property increases from DETA to PEHA. The binding energy values of inhibitor molecules are in the order PEHA > TETA > DETA which also supports the experimentally obtained results.

Bingul and co-workers studied the inhibition effects of methionine and tyrosine on the corrosion of Iron in HCl Solution by electrochemical and quantum-chemical method [160]. The quantum chemistry calculation for inhibition of corrosion has been performed with the 6-311G(d,p) basis set for methionine and tyrosine. The quantum chemical calculations were performed for methionine and tyrosine, as well as, for their protonated structures. The inhibition effect of methionine ion on Fe in HCl solution is better than that of tyrosine and is in agreement with experimental and theoretical data.

Kumari and Kumar have reported experimental and theoretical investigations of 3,3'-diamino dipropyl amine: highly efficient corrosion inhibitor for carbon steel in 2 N HCl at normal and elevated temperatures [161]. The theoretical study were performed by B3LYP using 6-31G(d) basis set and with the help of Gaussian 09, 6 Wallingford CT, the USA software. The adsorption of DADPA on carbon steel has been found from the data on global hardness, electronegativity, softness, chemical potential, ionization potential, maximum charge transfer, electron transfer, electrophilicity, nucleophilicity, electron releasing and accepting tendency, work function, back donation energy, proton affinity, metal inhibitor interaction, and binding energies. The strong adsorption of the inhibitor molecule was further supported by the suitable linear molecular configuration of DADPA, the high value of electronegativity, global softness parameter, and high negative value of interaction parameter.

Wang et al. studied experimental and theoretical investigation on corrosion inhibition of AA5052 aluminum alloy by L-cysteine in alkaline solution [162]. AA5052 aluminum alloy contains Mg, Mn, and Zn. The inhibition efficiencies of L-cysteine in 4 M NaOH solution were studied by polarization curves, electrochemical impedance spectroscopy, and quantum chemical calculation. The DFT calculations were performed using the Dmol3 package with numerical atomic orbital basis sets on Al (111) surface, double-numerical plus polarization (DNP) basis sets were used in the expansion of the Kohn-Sham orbitals and the orbital confining cut-off was set as 4.8 Å.
The adsorption of L-cysteine on an aluminum surface followed the Langmuir adsorption isotherm and the polarization curves showed that the L-cysteine acts as a cathodic inhibitor to inhibit the cathodic reaction.

The adsorption energy was calculated on the surface of Al(1 1 1) and the L-cysteine molecules found negative values. The adsorption energy decreases in the order, (e) < (a) < (d) < (c) < (b) indicates that inhibitor molecules adsorbs on the surface of aluminum instead of water molecules and the adsorption is mainly based on the reactive groups (Figure 4). The interaction between inhibitor molecules and Al surface was further understood by calculations of charge density (Figure 5).

Marcus et al. reported corrosion inhibition of locally de-passivated surfaces by DFT study of 2-mercaptobenzothiazole on copper [163]. They have studied the adsorption of the organic inhibitor 2-mercaptobenzothiazole (MBT) on the incompletely passivated or locally depassivated copper surface based on quantum chemical DFT calculations. They investigated quantum chemical DFT calculations on the adsorption of MBT in thione or thiolate forms on a model of the copper surface incompletely covered by a surface oxide film, Cu(111) surface covered by an ultrathin Cu$_2$O oxide film (Cu(111)||Cu$_2$O(111)). The calculation of DFT has been performed by periodic plane-wave basis set implemented in Vienna Ab initio Simulation Package (VASP) [70–73] with projector-augmented wave potentials using a 450 eV plane wave cutoff [74, 75]. Electron exchange and correlation terms were treated within the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) functional [76, 77]. They used a Methfessel–Paxton smearing [78] with smearing value of 0.1 eV. They started from Cu (111)||Cu$_2$O (111) model followed by the construction of the hole in the oxide consists in removing certain copper and oxygen atoms from the surface and interface oxide layers. The hole in the oxide has been generated by removing eight atoms of copper and two atoms of oxygen, which correspond to four copper and one oxygen atom in each oxide layer. This study suggests that the partially oxidized copper surface blocks the initiation of pitting corrosion by strong interaction with the MBT molecule.

Allah and Moustafa studied quantum chemical calculations for amino pyrazole derivatives as inhibitors of corrosion of zinc, copper, and α-brass in an aqueous acid chloride solution [164]. They have performed the quantum mechanical calculations using the Dewar LCAO-SCF MO semi-empirical method, MNDO (modified neglect of differential overlap). The inhibition efficiency of the amino pyrazole derivatives depends upon the position of the substituent group with respect to the pyrazole ring, that is, the para, meta, or ortho positions of the arylazo group.

![Figure 4](http://dx.doi.org/10.5772/intechopen.109523)

Figure 4. Optimized structure and adsorption energy modes of L-cysteine molecules on Al (1 1 1).
Zhang et al. reported QSAR study on N-containing corrosion inhibitors: Quantum chemical approach assisted by the topological index [165]. They have studied the inhibition efficiency used DFTB3LYP/6-31G* level using GAUSSIAN 98 program package to carried out $E_{\text{HOMO}}, E_{\text{LUMO}}$, energy gap, charge distribution, Dipole, topological index which refers to the steric hindrance of molecules.

Khadom has studied quantum chemical calculations of some amines corrosion inhibitors/copper alloy interaction in hydrochloric acid [166]. The quantum chemical calculations have been performed by Argus Lab 4.0.1 package, estimation by PM3 and AM1 method. The structural parameters, such as the frontier molecular orbital (MO), HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), dipole moment ($\mu$), and $\Delta N$ were calculated. The inhibition efficiency calculation performed by AM1 and PM3 are in agreement with the experimental results.

Liang and Gao reported electrochemical and DFT studies of $\beta$-amino-alcohols (1-diethylamino-propan-2-ol (EAP) and 1,3-bis-diethylamino-propan-2-ol (DEAP)) as corrosion inhibitors for brass [167]. The DFT calculation was carried out with the Gaussian 98 program, B3LYP, and the 6-311G** orbital basis sets. The interactions of the inhibitor molecules with the metal surface were studied by the frontier orbital energy such as $E_{\text{HOMO}}, E_{\text{LUMO}}$, and energy difference ($\Delta E$) and dipole moment ($\mu$). The $E_{\text{HOMO}}$ of DEAP ($-0.205$ a.u.) and EAP ($-0.222$ a.u.) and $\Delta E$ for EAP and DEAP are $-0.258$ and $-0.242$ a.u., respectively. The dipole moment ($\mu$) for DEAP and EAP are 2.32 and EAP 2.95, respectively. The theoretical calculations carried out for EAP...
and DEAP found that the inhibition efficiency of DEAP is higher than that of EAP which was in agreement with experimental results potentiodynamic curves and electrochemical impedance spectroscopy (EIS).

Elhenawy and co-workers studied the understanding the adsorption performance of two glycine derivatives (bicine (N,N-bis(2-hydroxyethyl)glycine) and tricine (N-(tri(hydroxymethyl)methyl) glycine) as novel and environmentally safe anti-corrosion agents for copper in chloride solutions: experimental, DFT, and MC studies [168]. The quantum chemical indices (QCIs) for bicine, tricine, and glycine were performed using the density functional theory (DFT) with DMol3 module in Materials Studio software (Accelrys Inc.), the generalized gradient approximation (GGA) of the BOP function was used through the double-numeric basis set (DNP 3.5).

The Monte Carlo (MC) simulations studies were performed on Cu (111) surface, COMPASS force field was done for minimum energy calculation. The energies were calculated from the geometry optimized structure (with the energy minima), Mulliken charges were computed at the GGA/DNP 4.4 level for the atoms in bicine, tricine, and glycine molecules. Tricine was found higher inhibition efficiency than bicine or glycine as tricine DE values (2.9194, 3.0000, and 0.5920) and lower than those of bicine (3.9193, 3.5117, and 1.0343) and glycine (4.6342, 4.1916, and 1.1731) in the gas, solvated, and protonated molecules, respectively. Also, the ΔN values found from theoretical data are the order tricine > bicine > glycine. The adsorption energy against the Cu (111) surface for tricine was found more than that for bicine from Monte Carlo (MC) simulations. The experimental results were in agreement with computational indicating higher efficiency for tricine over that for bicine.

5. Heterocyclic compounds as organic corrosion inhibitor

Heterocyclic compounds containing N, S, O, and P atoms, as well as compounds containing π-bonds and/or polar group that will provide protection of metals or alloys from corrosion. The heterocyclic compounds such as azoles, indoles, and aromatic rings can be used to provide corrosion protection.

The benzo imidazole [169] derivative, pyridine thiazole [170] compound, imidazole derivatives [171], phenanthroimidazole derivatives [172], and bis-benzothiazoles derivatives [173] can be used as corrosion inhibitor potency for mild steel and others. Pyridine, Indoles, [174–177], and Quinoline [44, 178–181] have shown sufficient potency for inhibition of iron, aluminum, carbon steel, N80 steel, mild steel, and zinc in different acidic media.

6. Conclusions

In this chapter, we discussed the theoretical and molecular modeling of organic compounds as corrosion inhibitors. The inhibition behavior of organic compounds was analyzed by density functional theory (DFT), Molecular dynamic simulation (MD), Monte Carlo (MC) simulations, quantitative structure-activity relationship (QSAR) modeling, etc. The computational chemistry studies of organic compounds as corrosion inhibitor save time and money. This approach is environmental friendly as there is no need for synthesis of organic compounds.
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References


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[28] Zhao JM, Zuo Y. Corrosion Science. 2002;44:2119-2130

[29] Ilevbare GO, Burstein GT. Corrosion Science. 2003;45:1545-1569


[56] Yang H-M. Molecules. 2021;26:3473


[60] Verma CB, Quraishi M, Singh A. Journal of the Taiwan Institute of Chemical Engineers. 2015;49:229-239


Organic Corrosion Inhibitors
DOI: http://dx.doi.org/10.5772/intechopen.109523


[128] Lukovits I, Kalman E, Zucchi F. Corrosion. 2001;57:3-8


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