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Recent Advances in Computational Design of Organic Materials for Corrosion Protection of Steel in Aqueous Media

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Additional information is available at the end of the chapter

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1. Introduction

1.1. Cost of corrosion

Cost of corrosion studies have been undertaken by several countries including the United States of America, the United Kingdom, Germany, Japan, India and China. In the United States (USA) the awareness of the cost of corrosion has been maintained at a high level. Professor Uhlig; the National Bureau of Standards (NBS), now the National Institute of Standards and Technology (NIST); Battelle Columbus Laboratories (BCL); and CC Technologies Laboratories (CC), along with NACE International and the Federal Highway Administration (FHWA), have contributed to the current knowledge on the cost of corrosion. In the United Kingdom (U.K.), the Hoar Committee has played a stellar role in estimating the cost of corrosion. In Japan, three approaches (Uhlig method, Hoar method, and NBS-BCL model) have been used. In India, the Uhlig method was followed in 1958, while the NBS-BCL model was adopted in 1986. Countries have attempted to relate the cost of corrosion to their gross national product (GNP). The common findings of these studies revealed that the annual cost of corrosion ranged from approximately 1 to 5 percent of Gross National Product (GDP) of each nation. In a widely-cited study (NACE Corrosion Costs Study) by the National Association of Corrosion Engineers, NACE, the direct cost of corrosion in the U.S. was estimated to equal \$276 Billion in 1998, approximately 3.1 % of GDP (Fig.1) [1]. A significant milestone in the effect of corrosion on the U.S. economy occurs in 2012 when the total cost of corrosion in the US exceeds \$1 trillion annually for the first time [2]. The annual cost of corrosion worldwide is estimated at \$ 2.2 Trillion (2010), which is about 3 % of the world's gross domestic product (GDP) of \$ 73.33 Trillion [3]. This amount is staggering and could be use to provide food and basic social

amenities to the world's poor which is part of the millennium development goals (MDGs) target by 2015.

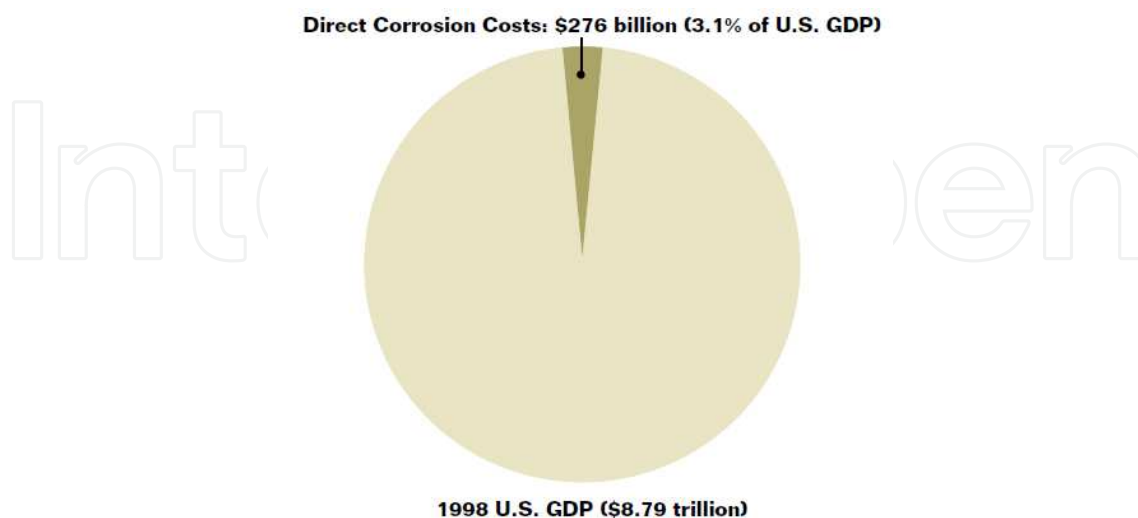


Figure 1. The impact of corrosion on the US economy.

1.2. The corrosion process

Corrosion can be defined in many ways. Some definitions are very narrow and deal with a specific form of corrosion, while others are quite broad and cover many forms of deterioration. The word corrode is derived from the Latin *corrodere*, which means “to gnaw to pieces.” The general definition of corrode is to eat into or wear away gradually, as if by gnawing. For the purpose of this chapter, corrosion may be defined as the deterioration of a metal or its properties due to its reaction with its environment. The environment consists of the entire surrounding in contact with the material (the emphasis in this chapter is on aqueous corrosion or corrosion in environments where water is present). It is the process that accounts for the reverse extractive metallurgy in which metals or metal components deteriorate upon reaction with harsh environments. The reaction may be chemical, electrochemical and/or mechanical. Corrosion is an undesirable process and represents the tendency of pure metals and alloys to return to thermodynamically more stable compounds. Thus, according to Shier, et al. [4], corrosion is defined as the reaction of an engineering material with its environment leading to a consequent deterioration in properties of material. Corrosion, its control and prevention is an interdisciplinary science which is served by many disciplines including Metallurgy, Electrochemistry, Material Science, Physics, Computational Chemistry and Chemical Engineering.

1.3. Corrosion mechanism

Corrosion processes are usually electrochemical in nature, having the essential features of a battery. When metal atoms are exposed to an environment containing water molecules, they can give up electrons, becoming themselves positively charged ions provided an electrical

circuit can be completed. Electrolytic corrosion consists of two partial processes: anodic (oxidation) and cathodic (reduction) reaction with consequent electron transfer between the two reactants. The two reactions occur at the same time and simultaneously upon a metal's surface. Thus, the metal is electrically charged and the rate of oxidation equals that of reduction. The loss of electron that is the usual manifestation of the corrosion process is a result of the anodic reaction (oxidation) in which the metal, M, loses electron (s) enter into ionic state as given in the equation below:



The anodic reaction may occur uniformly over the metal surface or may be localized at a specific region. If the dissolved metal ion can react with the solution to form an insoluble compound, then a build-up of corrosion products may accumulate at the anodic site.

In the absence of applied voltage, the electron(s) generated by the anodic reaction are consumed by the cathodic reaction, which is either hydrogen evolution reaction or the oxygen-reduction reaction.

The equation for the hydrogen-evolution reaction, is written as shown below:



This is the predominant cathodic reaction when corrosion occurs in low pH. The hydrogen evolution reaction can cause a serious problem since atomic hydrogen may enter the metal and cause embrittlement. Another important cathodic reaction is usually predominant in the neutral and alkaline media. The rate of this reaction depends upon the supply of oxygen to the metal surface. The equation for these reactions are as follows:



Eqs (3) and (4) represent the cathodic reaction in neutral and basic media respectively.

1.3.1. Uniform corrosion

Uniform attack or general corrosion occurs on the surface of a metal in the following way: If a metal is in contact with a conductive solution, some areas may become either anodic or cathodic sites. On the anode, the oxidation of the metal will occur, and the electrons supplied will be taken up at the cathode through the metal itself. Small currents will then flow from one to the other. The ions produced at the anode will migrate through the solution towards the

cathode, where they will form an oxide film with the product of the oxygen reduction. The location of the anode and cathode changes at all times, which makes the whole surface of the metal to corrode (Fig. 2).

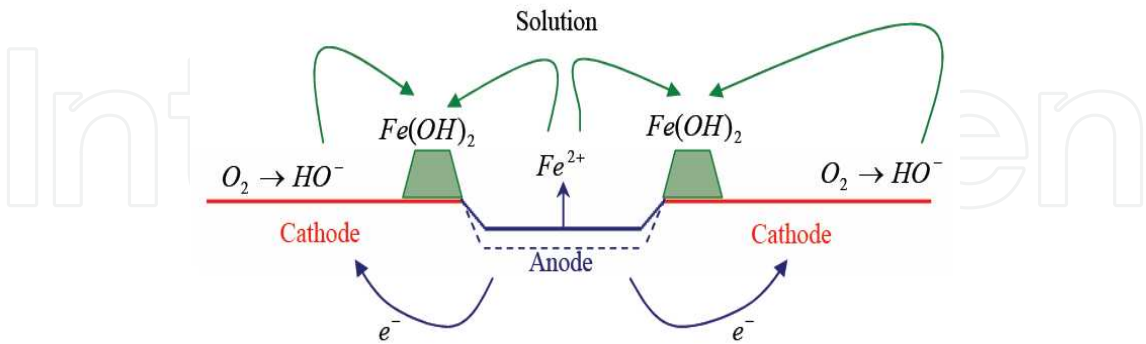


Figure 2. Uniform corrosion process of iron

1.3.2. Pitting

Pitting is a local form of corrosion (Fig. 3). This may occur at the surface of a metal due to the presence of an inhomogeneity (inclusion or break in a passive film). For this reason, aluminium alloys and stainless steel, which form passive films, are more likely to suffer from pitting. The cathode/anode area ratio as well as the pH will influence the process.

- In the pit (the anode) the oxidation of the metal takes place, releasing metal ions and electrons. The electrons then migrate to the cathode through the metal while the ions go into the solution. The presence of water then induces a further reaction known as hydrolysis:



- On the surface of the metal (the cathode), reduction of oxygen takes place:



Due to the hydrolysis of the metal ions into the pit, the conditions becomes acidic and the walls can not repassivate. The process is autocatalytic. Since the process is localized, the anode and cathode do not change their location. The pit itself will be small compared with the surface area of the metal. The anodic site will be small compared with the cathodic site, and the metal loss in the pit will be high. For this reason, the process is said to be under cathodic control, inducing a high level of penetration.

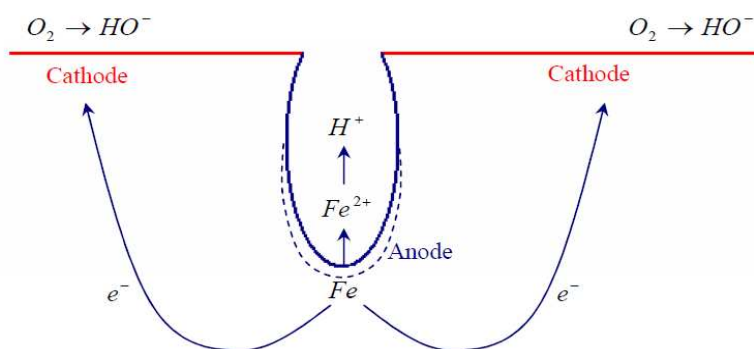


Figure 3. Pitting corrosion process of iron.

1.4. Corrosion inhibitors

A corrosion inhibitor may be defined, in general terms, as a substance that when added in a small concentration to an environment effectively reduces the corrosion rate of a metal exposed to that environment. Inhibition is used internally with carbon steel pipes and vessels as an economic corrosion control alternative to stainless steels and alloys, coatings, or non-metallic composites. A particular advantage of corrosion inhibition is that it often can be implemented or changed *in situ* without disrupting a process. The major industries using corrosion inhibitors are oil and gas exploration and production, petroleum refining, chemical manufacturing, heavy manufacturing, water treatment, and the product additive industries. The total consumption of corrosion inhibitors in the United States has doubled from approximately \$600 million in 1982 to nearly \$1.1 billion in 1998 [5]. US demand for corrosion inhibitors alone is forecast to rise 4.1 percent per year to \$2.5 billion in 2017, with volume demand approaching 1.7 billion pounds. Growth will be driven by higher oil and natural gas output, particularly from shale formations, as well as by increasing chemical production and an expanding economy. Additionally, robust increases in construction spending will support demand for corrosion inhibitors used in cement and concrete, industrial coatings, and metal applications. The industry will continue to invest in the development of new, less costly products such as organic corrosion inhibitors with better environmental profiles and improved performance.

The use of organic adsorption type corrosion inhibitors is a widely spread and cost-effective method to control carbon steel corrosion in the oil and gas production. The chemical functionalities employed in inhibitors formulation are very diverse and commercial inhibitors usually contain active components such as amides, amines, imidazolines, quaternary ammonium salts, etc. The inhibitors efficiency depends on a wide range of factors: flow patterns, solution chemistry, temperature, pressure, etc. The mechanism of action of inhibitors is difficult to establish and there is a large amount of research done on the subject.

Selecting a corrosion inhibitor, these must be considered [6]: (i). It should be synthesized conveniently from relatively cheap raw materials, *i.e.* (bio)organic precursors, or easily and cost-effectively extracted from natural resources. (ii). The presence of nitrogen, oxygen, sulfur, phosphorus and multiple bonds or aromatic rings in the inhibitor molecule is preferred. This

causes increased adsorption of the compound on the metal surface and to the enhancement of the inhibition efficiency. (iii). It should not cause production problems due to incompatibility with the system fluids, system conditions and other chemicals in the system. (iv). It should be non-toxic, not present a health risk to operators and maintenance personnel. (v). It should be acceptable to the environment, *i.e.* it should be environmentally friendly (“green”), if discharged with the effluent.

In the past two decades, the research in the field of “green” corrosion inhibitors has been addressed toward the goal of using cheap, effective molecules at low or “zero” environmental impact [7,8]. The following pie chart shows world consumption of corrosion inhibitors on a value basis as at 2008 (Fig. 4) [5]:

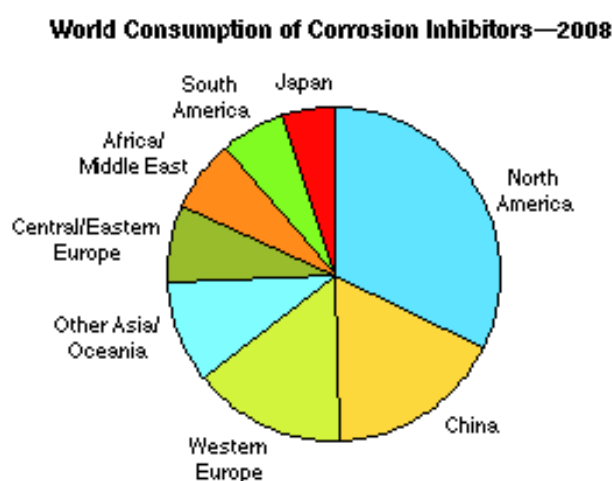


Figure 4. World consumption of corrosion inhibitors [5].

2. Brief theoretical background of Density Functional Theory (DFT)

The purpose of this section is to present a brief, but not an exhaustive, review of the basic theoretical background of the density functional theory. DFT, itself, has been described extensively elsewhere [9-11], but it is necessary to give a brief theoretical and computational concepts relevant to the application of DFT as a tool of choice for the computational design of organic corrosion inhibitors, which facilitates their adsorption onto metal and surfaces.

There are numerous quantum based approaches that have been applied to organic materials design including Hatree-Fock, Moller-Plesset, Coupled Cluster and Semi-empirical methods. However, the most popular for organic material design and calculations of chemical reactivity has been Density Functional Theory (DFT). The main reason for its popularity has been the relative accuracy with significantly lower computational cost compared to some of the other methods listed above.

The recent impact of density functional theory (DFT) in the development of quantum electro-chemistry is considerable, and can be linked to achievements at the end of the 1980s when

gradient-corrected and hybrid functional methods were introduced [12]. Based on the well-known Hohenberg-Kohn theorems (Kohn was awarded a Nobel Prize in physics in 1964 for his work on DFT in the same year that Pople was also awarded a Nobel Prize in the same field [13]), DFT focuses on the electron density, $\rho(r)$, itself as the carrier of all information in the molecular (or atomic) ground state, rather than on the single electron wave function, of which there is one per electron. Because the electron density arises from the collective contributions of all electrons, a considerable simplification of the many-bodied Schrödinger equation results, because of the reduction in the complexity (number of degrees of freedom) of the system. In summary, the Hohenberg-Kohn theorem establishes that the ground state of an electronic system is just a functional of the electronic density. In principle, one only needs the knowledge of the density to calculate all of the properties of a molecular system.

In DFT, the ground state total energy for an N-electron system is expressed in terms of the three-dimensional ground-state electronic density $\rho(r)$ and the external potential $v(r)$ in the form [14]:

$$E[\rho] = F[\rho] + \int dr \rho(r)v(r), \quad (8)$$

where $F[\rho]$ is the universal functional of Hohenberg-Kohn given by the sum of the electronic kinetic energy functional, and

$$N = \int dr \rho(r), \quad (9)$$

guarantees the proper normalization of the electron density.

A generalized DFT expression is [15]:

$$E_{DFT}[\rho] = T_S[\rho] + E_{ne}[\rho] + J[\rho] + E_{xc}[\rho] \quad (10)$$

where T_s is the kinetic energy functional (S denotes that the kinetic energy is obtained from a Slater determinant), E_{ne} is the electron-nuclear attraction functional, J is the Coulomb part of the electron-electron repulsion functional, and E_{xc} represents the exchange correlation functional. The dependence of each of these terms on the electron density, ρ , is represented by ρ in brackets following each term. Unfortunately, the exchange-correlation energy functional, which should be universal, is not known and practical (and approximate) solutions are obtained by the use of the so-called Kohn-Sham (KS) orbitals, which differ from other kinds of orbitals mostly by the fact that the sum of the squares of the occupied KS orbitals is the true electron density of the system, an assumption which is only approximated in other quantum chemical methods, such as Hartree-Fock.

The ground-state electronic density can be obtained from the solution of the Euler-Lagrange equation corresponding to the minimization of the energy given in Equ. (8), subject to the restriction by Equ. (9), that is,

$$\mu = \left(\frac{\delta E}{\delta \rho(r)} \right)_v = v(r) + \frac{\delta F}{\delta \rho(r)}, \quad (11)$$

where μ , the undetermined Lagrange multiplier, is the chemical potential that measures the escaping tendency of the electrons from a system. Electrons flow from places with higher chemical potential to places with lower chemical potential up to the point in which μ becomes constant throughout space. A brief history of DFT is presented in Table 1.

Year	Event
1926	Old DFT developed by Thomas-Fermi theory.
50's and 60's	Slater and co-workers develop $X\alpha$ as crude Kohn-Sham Local density Approximations (KS-LDA).
1965	Modern DFT begins with Kohn-Sham equations. By introducing orbitals, 99% of the kinetic energy was gotten right, accurate $\rho(r)$, and only need to approximate a small contribution, $EXC[\rho]$.
1965	Kohn-Sham (KS) also suggested local density approximation (LDA) and gradient expansion approximation.
1993	More modern functionals i.e. Generalized Gradient Approximations (GGA's) and Hybrids shown to be usefully accurate for thermochemistry.
1998	Kohn and Pople won Nobel prize in Chemistry.
2010	DFT applied in solving problems in materials science, geology, soil science, astrophysics, protein folding etc.

Table 1. Brief History and Timelines of DFT

3. DFT based chemical reactivity indicators

3.1. Global reactivity parameters

The design of organic corrosion inhibitors for metal protection (those that bind covalently to metal surfaces in order to prevent them from corroding), requires the use of chemical descriptors that encapsulate how covalently reactive a given organic molecule is. Quantum chemical descriptors are related to the electronic structure of organic materials and to the chemical mechanisms that are involved in covalent bond formation between them and the metal surfaces. Many efficient corrosion inhibitors are organic compounds rich in heteroatoms such as nitrogen, oxygen, sulfur and π -bonds. It has been reported that organic inhibitors bearing both nitrogen and sulphur atoms on the same molecular structure are more effective than inhibitors having only nitrogen atom. It is generally accepted that corrosion inhibition

efficiency of organic compounds is related to their adsorption properties. The adsorption of these molecules depend mainly on certain physicochemical properties of the inhibitor molecule such as, functional groups, steric factor, aromaticity, electron density at the donor atoms and p-orbital character of donating electrons, electronic structure of the molecules and the strength of interaction between the inhibitor and the metal surface. The organic inhibitor should not only donate electrons to the unoccupied d- orbital of the metal, but can also accept electrons from the d-orbital of the metal leading to the formation of a feed-back bond

The basic relationship of the density functional theory of chemical reactivity is, precisely, the one established by Parr, Donnelly, Levy and Palke [15], that links the chemical potential (μ) of DFT with the first derivatives of the with respect to the number of electrons, and therefore with the negative of the electronegativity χ

$$\mu = \left(\frac{\delta E}{\delta N} \right)_v = -\chi. \quad (12)$$

The next fundamental aspect comes from the identification of the concept of chemical hardness with the second derivative of the energy with respect to the number of electrons [16], that is,

$$\eta = \left(\frac{\delta^2 E}{\delta N^2} \right)_v = \left(\frac{\delta \mu}{\delta N} \right)_v. \quad (13)$$

In accordance with the earlier work of Iczkowski and Margrave [17], it should be noted that, when assuming a quadratic relationship between E and N and in a finite difference approximation, Equ. (12) may be written as:

$$\chi = -\mu = \left(\frac{I + A}{2} \right) \quad (14)$$

In terms of the energies of HOMO and LUMO molecular orbitals, hardness is given as [18]:

$$\eta = \frac{I - A}{2}, \eta = -\frac{E_{LUMO} - E_{HOMO}}{2} \quad (15)$$

where I and A are the ionization potential and electron affinity, respectively, thereby recovering the electronegativity definition of Mulliken [19]. Moreover, a theoretical justification was provided for Sanderson's principle of electronegativity equalization, which states that when two or more atoms come together to form a molecule, their electronegativities become adjusted to the same intermediate value [20].

The global softness (S), is the inverse of global hardness and is given as [21]:

$$S = \frac{1}{2\eta} = \left(\frac{\partial N}{\partial \mu} \right)_{v(r)} \quad (16)$$

The global electrophilicity index (ω) was introduced by Parr et al. [22] and is given by:

$$\omega = \frac{\mu^2}{2\eta} \quad (17)$$

Using the parabolic model, it was shown that global electrophilicity index (ω), can also be written as [10]:

$$\omega = \frac{(I + A)^2}{8(I + A)} \quad (18)$$

The electron charge transfer, ΔN , from base B to acid A, and the associated energy change ΔE is given as [23]:

$$\Delta N = \frac{\mu_B - \mu_A}{2(\eta_A + \eta_B)} \text{ and } \Delta E = -\frac{(\mu_B - \mu_A)^2}{2(\eta_A + \eta_B)} \quad (19)$$

Substituting the subscripts A and B by metal and mol to designate a metal surface and a molecule, respectively, and replacing the μ by $-\chi$ gives:

$$\Delta N = \frac{\chi_{metal} - \chi_{mol}}{2(\eta_{metal} + \eta_{mol})} = \frac{\Phi - \chi_{mol}}{2\eta_{mol}} \quad (20)$$

$$\Delta E = -\frac{(\chi_{metal} - \chi_{mol})^2}{4(\eta_{metal} + \eta_{mol})} = -\frac{(\Phi - \chi_{mol})^2}{4\eta_{mol}} \quad (21)$$

In the second equality of Eqs 20 and 21, the electronegativity of metal surface is replaced by the work function for metal surface, Φ .

3.2. Local reactivity parameters

The local reactivity of organic inhibitors can be analyzed through an evaluation of the Fukui indices [24]. These are measures of the chemical reactivity, as well as an indication of the reactive regions and the nucleophilic and electrophilic behavior of the molecule. The density functional definition of the Fukui function provides a firm foundation of the frontier-electron

theory [25, 26]. Using a scheme of finite difference approximations from Mulliken population analysis of atoms in inhibitors and depending upon the direction of electron transfer we have:

$$f_k^+ = q_k(N+1) - q_k(N) \text{ (for nucleophilic attack)} \quad (22)$$

$$f_k^- = q_k(N) - q_k(N-1) \text{ (for electrophilic attack)} \quad (23)$$

$$f_k^o = \frac{q_k(N+1) - q_k(N-1)}{2} \text{ (for radical attack)} \quad (24)$$

where q_k is the gross charge of atom k in the molecule i.e. the electron density at a point r in space around the molecule. N corresponds to the number of electrons in the molecule, with $N+1$ corresponding to a singly-charged anion, with an electron added to the LUMO of the neutral molecule; and $N-1$ corresponding to singly-charged cation with an electron removed from the HOMO of the neutral molecule.

The local softness [25] is defined as:

$$s(r) = \left[\frac{\partial n(r)}{\partial \mu} \right]_{v(r)} \quad (25)$$

and this equation yields the global softness upon integration:

$$S = \int s(r) dr. \quad (26)$$

The relationship between the local softness and the Fukui function,

$$s(r) = Sf(r), \quad (27)$$

reflects that these quantities contain the same information about the relative site reactivity in a molecule.

A number of computational methods are available for the calculation of theoretical descriptors. A list of commonly used quantum chemical reactivity descriptors is given in Table 2.

Descriptors	Explanation
Global quantum chemical descriptors	
E_{HOMO}	Energy of the highest occupied molecular orbital
E_{LUMO}	Energy of the lowest unoccupied molecular orbital
$IP(\approx -E_{HOMO})$	Ionization potential: Removing an electron from a molecular system X ($X \rightarrow X^+ + e^-$)
$EA(\approx -E_{LUMO})$	Electron affinity: Attaching an additional electron to a molecular system X ($X + e^- \rightarrow X^-$)
$\mu = \left(\frac{\delta E}{\delta N}\right)_v$	Chemical potential, defined as the change in electronic energy E upon change in total number of electrons N
$\chi = -\mu \approx -1/2(E_{HOMO} + E_{LUMO})$	Absolute electronegativity
$\eta = -\left(\frac{\delta \mu}{\delta N}\right)_v \approx -(E_{HOMO} - E_{LUMO})$	Molecular hardness, defined as the change in chemical potential μ upon change in total number of electrons N
$S = \frac{1}{2\eta}$	Molecular softness
α	Molecular polarizability; Note that molecules arrange themselves towards a state of minimum polarizability and maximum hardness
$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta}$	Electrophilicity index
Charge distribution	
$QA(r)$	Net atomic charges (at atom r)
PSA	Polar surface area, describing the spacial surface density distribution
μ	Molecular dipole moment
Site specific molecular descriptors (Local quantum descriptors)	
$f^+(r) = \left(\frac{\delta \rho(r)}{\delta N}\right)_{v(r)}^+ \approx \rho_{N+1}(r) - \rho_N(r)$	Electrophilic Fukui function, defined as the change in electron density ρ at atom r upon addition of electrons to the system (N = number of electrons)
$f^-(r) = \left(\frac{\delta \rho(r)}{\delta N}\right)_{v(r)}^- \approx \rho_N(r) - \rho_{N-1}(r)$	Nucleophilic Fukui function, defined as the change in electron density ρ at atom r upon removal of electrons from the system (N = number of electrons)
$\omega(r) = \omega \times f^+(r)$	Local electrophilicity index
$\omega(r) = \omega \times f^-(r)$	Local nucleophilicity index
$\Delta f(r) = f^+(r) - f^-(r)$ or $\Delta f(r) \approx \rho_{LUMO}(r) - \rho_{HOMO}(r)$	Reactivity-selectivity descriptor or dual descriptor, while $f^+(r)$ measures reactivity towards nucleophilic and $f^-(r)$ towards electrophilic attacks; therefore, electrophilic sites are identified by $\Delta f(r) > 0$. ρ_{LUMO} and ρ_{HOMO} are the electron densities of the LUMO and HOMO orbitals, respectively.

Table 2. Important molecular descriptors used to model chemical reactivity and molecular characterization/design of organic materials for metallic protection.

4. Commonly used DFT softwares

There are a wide variety of computational chemistry packages available to suit the needs of most researchers in the area of organic corrosion inhibitor modeling. They differ in terms of price, popularity and theoretical methods available. The list below covers some of the most popularly used in the areas of material design and characterization of organic corrosion inhibitors. It is not an endorsement of any software by the author and the decision to use any of the listed software is purely that of the reader. Commonly used softwares for quantum chemical computation is presented in Table 3.

4.1. TURBOMOLE

Turbomole is a quantum chemical program package, initially developed in the group of Prof. Dr. Reinhart Ahlrichs at the University of Karlsruhe and at the Forschungszentrum Karlsruhe. The package has an exceptional DFT subsystem.

4.2. GAUSSIAN

This is probably the most popular computational chemistry package in use today. It has over 42 years of history and has numerous publications. It was originally developed by Pople in the early 1970's. It is marketed by Gaussian Inc. The code uses Gaussian orbitals to build up the basis sets. In its original form it was primarily a Hartree- theory code. However, today it offers a range of capabilities including DFT, Semi-empirical, Hybrid QM/MM and numerous other approaches. Starting from the basic laws of quantum mechanics, Gaussian predicts the energies, molecular structures, and vibrational frequencies of molecular systems, along with numerous molecular properties derived from these basic computation types.

4.3. GAMESS

GAMESS is a program for *ab initio* molecular quantum chemistry. Briefly, GAMESS can compute SCF wavefunctions ranging from RHF, ROHF, UHF, GVB, and MCSCF. Correlation corrections to these SCF wavefunctions include Configuration Interaction, second order perturbation Theory, and Coupled-Cluster approaches, as well as the Density Functional Theory approximation.

4.4. PC GAMESS

PC GAMESS is a freely available *ab initio* and DFT computational chemistry program developed to offer high performance on Intel-compatible x86, AMD64, and EM64T processors. It was initially based on the free GAMESS(US) program sources but extends its functionality in some important areas. PC GAMESS has very efficient MP2 energy and gradient modules.

4.5. ORCA

ORCA is a flexible, efficient and easy-to-use *general* purpose tool for quantum chemistry written by F. Neese, with contributions from U. Becker, D. Ganiouchine, S. Koßmann, T.

Petrenko, C. Riplinger and F. Wennmohs. It offers specific emphasis on spectroscopic properties of open-shell molecules and features a wide variety of standard quantum chemical methods ranging from semiempirical methods to DFT to single- and multireference correlated ab initio methods. It can also treat environmental and relativistic effects.

4.6. CASINO

CASINO is a code for performing quantum Monte Carlo (QMC) electronic structure calculations for finite and periodic systems. The code is developed by the Theory of Condensed Matter - Quantum Monte Carlo (TCM - QMC) group of Richard Needs at the University of Cambridge largely by Mike Towler, considerably assisted from 2002 by Neil Drummond and from 2004 by Pablo López Ríos.

4.7. CRYSTAL

CRYSTAL can be used to compute the electronic structure of periodic systems within Hartree Fock and density functional theory. A variety of exchange functionals (LDA, VBH, BECKE, PWGGA, PBE) and correlation functionals (VWN, PWLSD, PZ, VBH, LYP, P86, PWGGA, PBE) are currently available, as well as the hybrid functionals, B3LYP and B3PW. Restricted closed shell, restricted open shell and unrestricted Hartree-Fock methods may be used.

4.8. NWCHEM

NWChem is a computational chemistry package that is designed to run on high-performance parallel supercomputers as well as conventional workstation clusters. It aims to be scalable both in its ability to treat large problems efficiently, and in its usage of available parallel computing resources.

4.9. ABINIT

ABINIT is a package whose main program allows one to find the total energy, charge density and electronic structure of systems made of electrons and nuclei (molecules and periodic solids) within Density Functional Theory (DFT), using pseudopotentials and a planewave basis. ABINIT also includes options to optimize the geometry according to the DFT forces and stresses, or to perform molecular dynamics simulations using these forces, or to generate dynamical matrices, Born effective charges, and dielectric tensors. Excited states can be computed within the Time-Dependent Density Functional Theory (for molecules), or within Many-Body Perturbation Theory (the GW approximation).

4.10. MOPAC

MOPAC (Molecular Orbital PACKage) is a semiempirical quantum chemistry program based on Dewar and Thiel's NDDO approximation used for the prediction of chemical properties and modeling of chemical reactions. It is used by chemists and biochemists for both research and teaching, and runs on Windows and Linux platforms.

4.11. VIEWMOL

Viewmol is an open source graphical front end for computational chemistry programs. It is able to graphically aid in the generation of molecular structures for computations and to visualize their results. It can read and write many known file types, including *Turbomole* files

4.12. ADF

Amsterdam Density Functional (ADF) This package has over a 32 year track record of development. It was originally written by Baerends (Vrije University, Amsterdam) and Ziegler (University of Calgary). It is based on Slater atomic orbitals and has the ability to work with a range of different systems; surfaces, periodic cells, and gas phase molecules.

4.13. DMol

This code was originally developed by Delley (Paul Scherrer Institute) in late 1980's. Like ADF and Gaussian it uses localized orbitals to describe the electron density. However, unlike these codes the basis sets are numerical, making the code very fast. However, the trade off is that the code has a finite level of accuracy as the calculations cannot be made more accurate by progressively adding basis functions. It has been successfully used for solids, surfaces and gas phase molecules. It is marketed by Accelrys as part of their Material studio software suite and has been used in over 700 publications.

SOFTWARES-QUANTUM MECHANICS	
NAME	DESCRIPTION
ADF	Quantum Mechanics (QM)
ABINIT	QM (Molecular and Periodic Systems)
AMPAC	QM (Semi-empirical)
CRYSTAL	QM for Periodic Systems
Dalton	QM Specializing in magnetic/electric properties
Discovery Studio	QM & MM/MD suite of software with a user-friendly Interface for Life Sciences
GAMESS-US	QM
Gaussian	QM
Jaguar (Qsite)	QM (QM/MM)
Materials Studio	MM/MD & QM suite of software with a user-friendly GUI for Materials Sciences
MOLPRO	QM (specializing in high-level calculations)
NWChem	QM
SIESTA	QM specializing in electron transport and Solids
VASP	QM specializing in QMD
MM= Molecular mechanics, QMD= Quantum Molecular Dynamics	

Table 3. Commonly used softwares for quantum mechanics and their descriptions.

5. Some recent studies of inhibitor design using DFT reactivity indices

In designing new corrosion inhibitors from organic compounds using DFT, the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), the HOMO-LUMO energy gap, the dipole moments and molecular polarizability are the most important electronic parameters to be considered. As reported by several researchers [27-29], excellent corrosion inhibitors are usually those organic compounds which do not only offer electrons to unoccupied orbital of the metal, but also accept free electrons from the metal. It is also well established in the literature that the higher the HOMO energy of the inhibitor, the greater the trend of offering electrons to unoccupied d-orbital of the metal, and the higher the corrosion inhibition efficiency [30, 31]. In addition, the lower the LUMO energy, the easier the acceptance of electrons from metal surface, as the LUMO-HOMO energy gap decreased and the efficiency of inhibitor improved. Furthermore, the dipole moment μ is a measure of the polarity of a covalent bond, which is related to the distribution of electrons in a molecule [32]. Although literature is inconsistent with the use of μ as a predictor for the direction of a corrosion inhibition reaction, it is generally agreed that the large values of μ favour the adsorption of inhibitor onto a metal surface [33]. The polarizability $\langle\alpha\rangle$ is an indicator of the linear response of the electron density in the presence of an infinitesimal electric field, which depends on the second derivative of energy with respect to the electric field. The higher values of $\langle\alpha\rangle$ facilitate the strong adsorption process of corrosion inhibitors onto metallic surfaces and hence, high inhibition efficiency [34].

The work of Parr, Pearson and others [35, 36], within the framework of Density Functional Theory (DFT), has established a general rule predicting the stability of the electronic structure of molecules. The general rule of this new paradigm is that the index of chemical reactivity and stability of a molecule is its global hardness, η . Increase in hardness increases the movement of the system towards a more stable configuration and when a chemical species moves away from its equilibrium configuration its hardness value decreases. When a system evolves towards a state of greater hardness, its stability increases. When a system evolves towards the state of lower hardness, its stability decreases. η , is again used as an index of chemical reactivity. The higher the value of η , the lesser is its reactivity. The global softness, S , the inverse concept of hardness, is useful for a straightforward prediction of chemical reactivity. The soft molecules undergo changes in electron density more easily than the hard molecules and are more reactive than the hard molecules. A molecule having higher S value is more reactive than a molecule having smaller S value. In general, it can be said that the increase in softness increases chemical reactivity and increase in hardness decreases chemical reactivity. Thus in the design of new corrosion inhibitors using DFT from a family of organic molecules with related structures, a molecule with lower value of hardness and high value of softness is expected to have a high inhibition efficiency when its adsorbed onto a metal surface.

Other useful reactivity and selectivity indices to be considered when designing new corrosion inhibitors using DFT include: the fraction of electrons transferred from the inhibitor molecule to the metal surfaces, the partial atomic charges and the condensed Fukui functions. The number of electrons transferred (ΔN) indicates the tendency of a molecule to donate electrons. The higher the value of ΔN is, the greater the tendency of a molecule to donate electrons to the electron poor species. In the case of corrosion inhibitors, a higher ΔN implies a greater tendency

to interact with the metal surface (i.e., a greater tendency to adsorb on the metal surface) [23]. Beside reactivity indicators, several molecular properties are good indicators of selectivity (i.e., the regions on the molecule on which certain type of reactions are likely to occur) and include the partial atomic charges and the condensed Fukui functions. The atom with the highest negative partial charge is considered a possible site for an attack by electron deficient species [37]. The condensed Fukui functions are local selectivity descriptors. These functions inform about the centers in a molecule on which nucleophilic, electrophilic and radical reactions are most likely to occur. The Fukui functions for the electron rich centers (i.e., atoms susceptible to electrophilic attack) and electron deficient centers (i.e., atoms that are susceptible to nucleophilic attack) are often estimated using the finite difference approximation approach [38]. The preferred site for nucleophilic attack is the atom (or region) in the molecule where f^- has the highest value while the site for electrophilic attack is the atom (or region) in the molecule where the value of f^+ is the highest.

Computational methods have evolved as important tools in corrosion inhibitor design during the last two decade, as calculations can provide a large amount of information of large numbers of compounds within reasonable timeframe. Results from such studies can be used as suitable starting points for further experimental studies. Computational methods can also be important tools in the development of more suitable compounds to be used for metal protection, starting from already available compounds and through structural modifications identify derivatives with improved metal protection efficacy. Recently, there are lots of studies in the literature on the computational study of organic materials useful for metal protection. The goal of these studies is to gain insights at the molecular level on the interaction of these organics with metal surfaces. This important approach is very vital in the design of new and effective corrosion inhibitors for industrial applications especially in the oil and gas sectors. Some of the recent researches are reviewed below. They are by no mean exhaustive as excellent review exist elsewhere [39].

5.1. DFT theoretical study of 7-R-3methylquinoxalin-2(1H)-thiones (R=H; CH₃; Cl) as corrosion inhibitors in hydrochloric acid

Quantum chemical approach at DFT/B3LYP/6-31G(d,p) level of theory was used to calculate some structural and electronic properties of three quinoxaline derivatives to ascertain the correlation between their experimental corrosion inhibition efficiencies on mild steel in acidic media and some of the computed parameters [40]. The global reactivity indicators show that Me-Q=S is a better inhibitor than Q=S and Cl-Q=S, respectively. Quantum chemical parameters calculated include E_{HOMO} , the dipole moment (μ), electronegativity (χ) and the amount of electrons transferred from organic inhibitor to the metal surface (ΔN) e.t.c. The high value of electron donor capacity of Me-Q=S when compared to Q=S and Cl-Q=S makes it more effective among the three compounds investigated. The substitution of the methyl group by the chlorine group in C7 position leads to a notable decrease in the adsorption capacity of the inhibitors which is as a result of the electronic effect of the substituent directly attached to the phenyl ring (Fig. 5). The Fukui functions and the electron density distribution showed that the S atom was probably the main adsorption site.

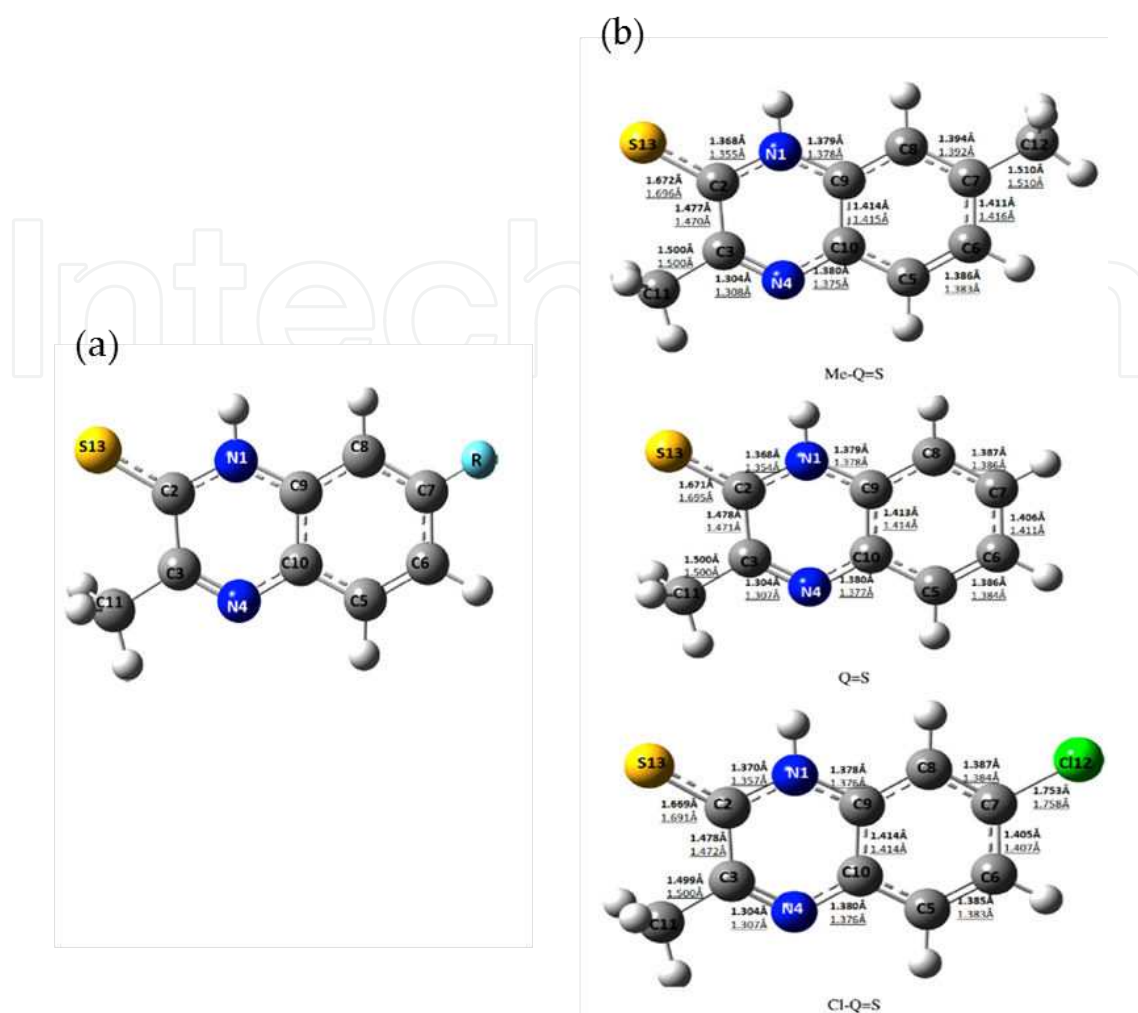


Figure 5. (a) The 7-R-3methylquinoxalin-2(1H)-thiones (R=H; CH₃; Cl) (b) Selected geometrical parameters of the compounds calculated at in gas (bold) and aqueous phases (underlined) [Adapted from ref. [40]].

5.2. DFT theoretical studies of antipyrine Schiff bases as corrosion inhibitors

Quantum chemical calculations based on DFT/B3LYP/6-31G level were performed to find the relation between the molecular structure of the inhibitor and the inhibition efficiency of some schiff bases namely: (benzylidene amino)antipyrine (a), 4-hydroxy 3-(benzylidene amino)antipyrine (b), 2-hydroxy 3-(benzylidene amino)antipyrine (c), and 2-hydroxy 3-(naphthylidene amino)antipyrine (d) [41]. The quantum chemical parameters confirmed that the replacement of phenyl group by naphthyl group increases the inhibition efficiency of the inhibitor toward the metal surface which means that the inhibitor (d) had higher inhibition efficiency than the inhibitor (c). Moreover, the substitution of the hydrogen atom of phenyl ring by a hydroxyl group increases the adsorption of the inhibitor toward the metal surface which means that the inhibitors (c) and (b) had higher inhibition efficiency than inhibitor (a). Also the substituent hydroxyl group in the ortho position in the case of inhibitor (c) favored more the adsorption of the inhibitor than that in the para position. This means that the inhibition efficiency of

inhibitor (c) is higher than that of inhibitor (b). It is concluded from the calculations that the real controlling quantum factors to determine the inhibition efficiency of antipyrine inhibitors are energy gap (ΔE), total negative charges (TNC), and softness (S) of the molecules (Fig. 6).

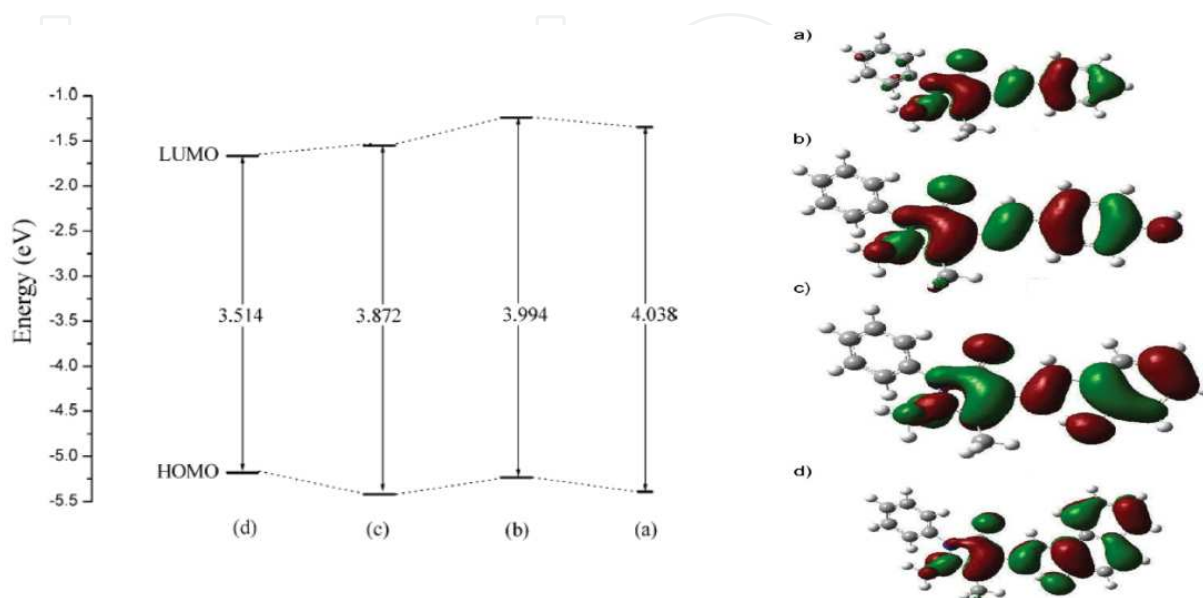


Figure 6. (a) Correlation diagram and energy gap values of inhibitors (a-d); (b) HOMO orbitals of inhibitors (a-d) [Adapted from ref. [41]].

5.3. Theoretical evaluation of corrosion inhibition performance of imidazoline compounds with different hydrophilic groups

Corrosion inhibition performance of four 1-R-2-undecyl-imidazoline compounds ($R = \text{CH}_2\text{COOH}$ (A), $\text{CH}_2\text{CH}_2\text{OH}$ (B), $\text{CH}_2\text{CH}_2\text{NH}_2$ (C) and H (D)) for carbon steel was evaluated by quantum chemistry and molecular mechanics methods [42]. The quantum chemical study such as E_{HOMO} , E_{LUMO} , and global reactivity parameters indicates that the inhibition efficiency of the four inhibitors followed the order of $A > B > C > D$. Further investigation using molecular mechanics method showed that these inhibitor molecules would form a self assembled monolayer (SAM) on the Fe surface, and related parameters such as alkyl chain distance, title angle, interaction energy, and cohesive energy were compared. These parameters implies that the SAM became less compact and stable from molecules A to D, and the interaction between the SAM and the Fe surface was also weakened. These results denote the same inhibition efficiency order of the four inhibitors revealed by quantum chemistry calculation. The results by the two simulation methods were validated by previously reported experimental results. The results were more reliable than that obtained via each single method, and could provide a model for the design of new organic corrosion inhibitors.

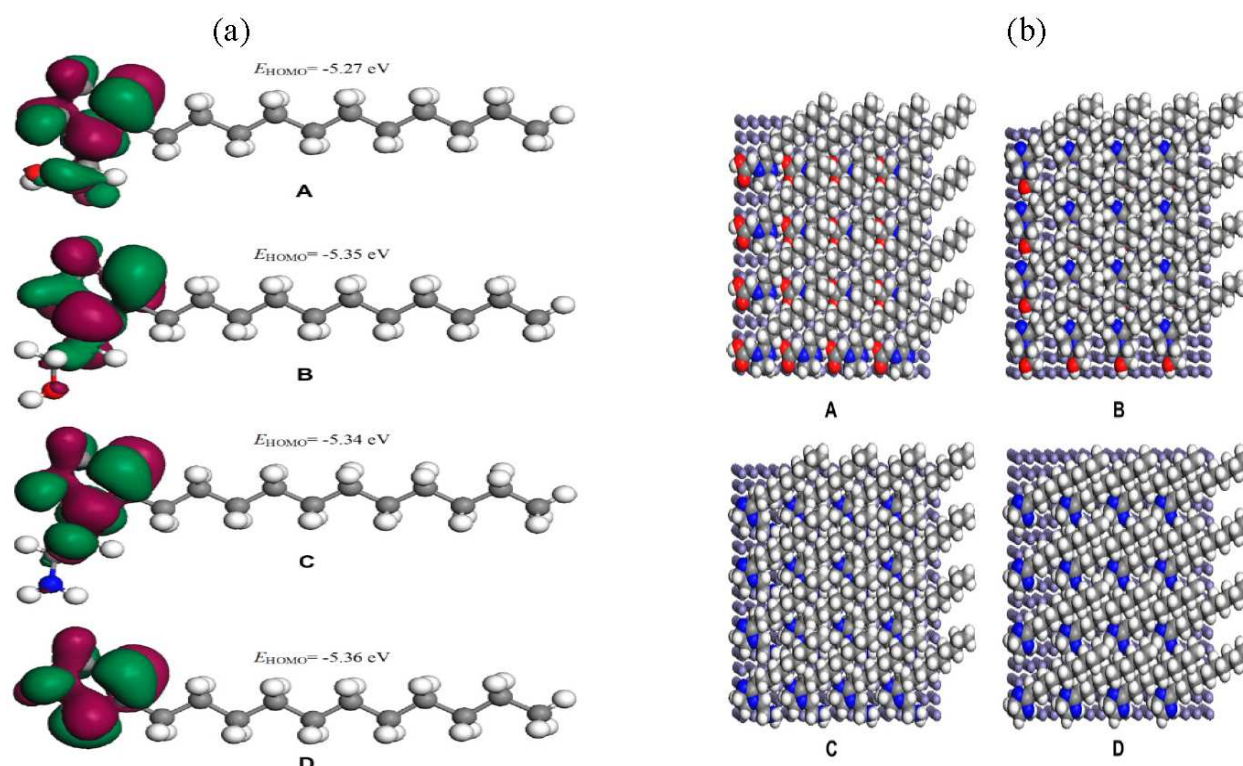


Figure 7. (a) HOMO of molecules A-D; (b) Optimized SAM for A-D molecules formed on Fe (0 0 1) surface [Adapted from ref. [42]].

5.4. Theoretical evaluation of the inhibition properties of two thiophene derivatives on corrosion of carbon steel in acidic media.

The density functional theory at the B3LYP/6-311G++(d,p) basis set level calculations were performed on two thiophene derivatives used as corrosion inhibitors, namely 2-methylthiophene (MT) and 2-(aminomethyl)thiophene (AMT) (Fig. 8), to investigate the correlation between its molecular structure and the corresponding inhibition efficiency (IE%) [43]. The inhibition efficiency is closely related to the quantum chemical parameters, E_{HOMO} , E_{LUMO} , ΔE , μ , η , and ΔN for the protonated inhibitors. It was shown that AMT molecule has the highest inhibition efficiency, which is probably due to the presence of amino group. Both inhibitors had a considerable tendency for protonation and the most probable site of protonation was the α -position of the thiophene ring. Finally, this study confirms the reliability of the quantum chemical methods to study the inhibition of corrosion of metal surface.

5.5. Theoretical study on relationship between structure of mercapto-triazole derivatives and inhibition performance

Relationships between corrosion inhibition efficiency of five kinds of mercapto-triazole inhibitors and their molecular electronic properties were theoretically studied at the level of DFT/B3LYP with 6-31+G (d, p) base sets [44]. The detailed studies revealed that corrosion inhibition efficiency and frontier orbital energy level E_{HOMO} show close correlation. The HOMO

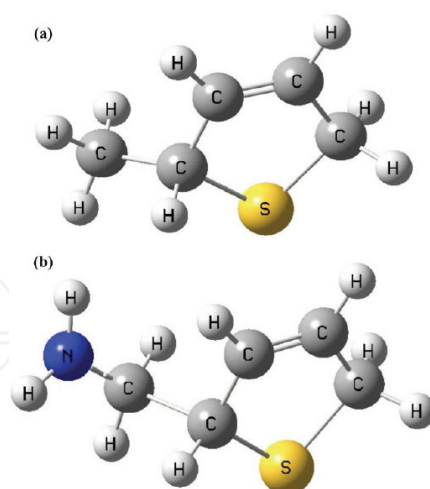


Figure 8. Optimized structures of molecules (a=MT, b=AMT) [Adapted from ref. [43]].

orbital were mainly delocalized around the triazole ring. By analyzing the molecular electrostatic potential surfaces for each molecule, it was found that most of the negative potential is concentrated on the triazole ring R2 and a small part on benzene ring R1. R2 plays a main role and R1 plays a synergistic role during the process of inhibitor adsorption on a metal surface. Further investigation indicates that the interaction energies between corrosion inhibitors and Fe(100) are positively correlated with corrosion inhibition efficiencies. It was theoretically predicted that the main structure of the inhibitor (rings R2 and R1) plays an important role for these inhibitors, as does the HOMO energy. Based on this information, attempt were made to design some superior homologous corrosion inhibitors. Example of the new designed inhibitor is given in Fig. 9.

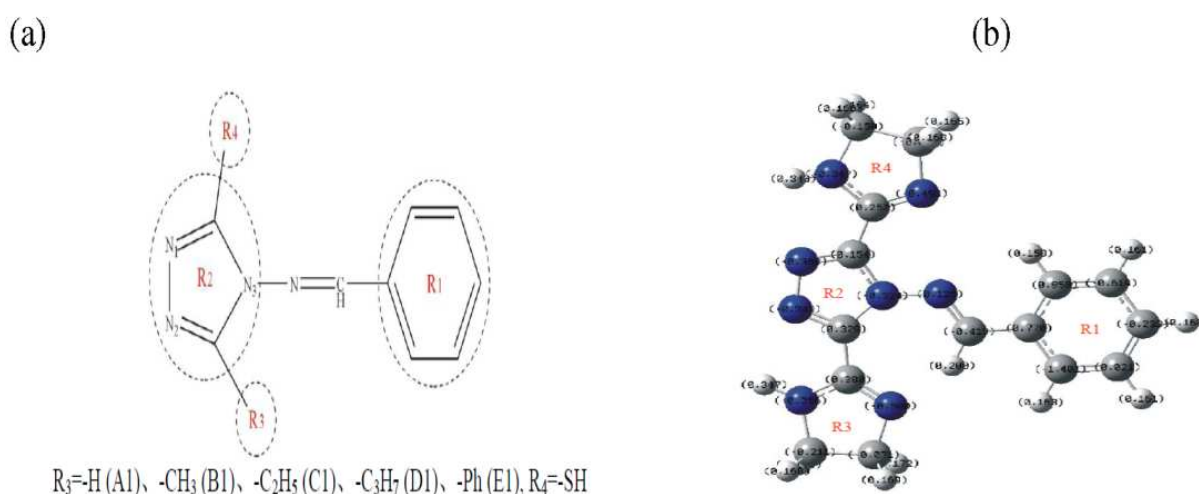


Figure 9. (a) The five mercapto-triazole inhibitors studied; (b) Optimized structure of the new designed inhibitor [Adapted from ref. [44]].

5.6. Experimental and theoretical studies for corrosion inhibition of carbon steel by imidazoline derivative in 5% NaCl saturated $\text{Ca}(\text{OH})_2$ solution

Quantum chemical calculations and molecular dynamic (MD) simulations were applied to analyze the experimental data and elucidate the adsorption behavior and inhibition mechanism of 1-[N,N'-bis(hydroxyethylether)-aminoethyl]-2-stearicimidazoline (HASI) for carbon steel in 5% NaCl saturated $\text{Ca}(\text{OH})_2$ solution [37]. Density functional theory (DFT) calculations suggest that the N=C-N region in imidazoline ring is the most active reaction site for the inhibitor adsorption on metal surface via the donor–acceptor interactions between the lone electron pairs on nitrogen atoms together with the π -electrons of heterocyclic and the vacant d-orbital of iron atoms. The adsorption of inhibitor on three typical surfaces (Fe (1 0 0), Fe_2O_3 (1 1 0) and Fe_3O_4 (1 0 0)) takes nearly parallel to the surface so as to maximize its contact with the surface, as shown as the MD simulations (Fig. 10). The experiments incorporating the theoretical calculation and MD simulation can provide an insight into the understanding of interactions between the inhibitor molecules and the carbon steel surface.

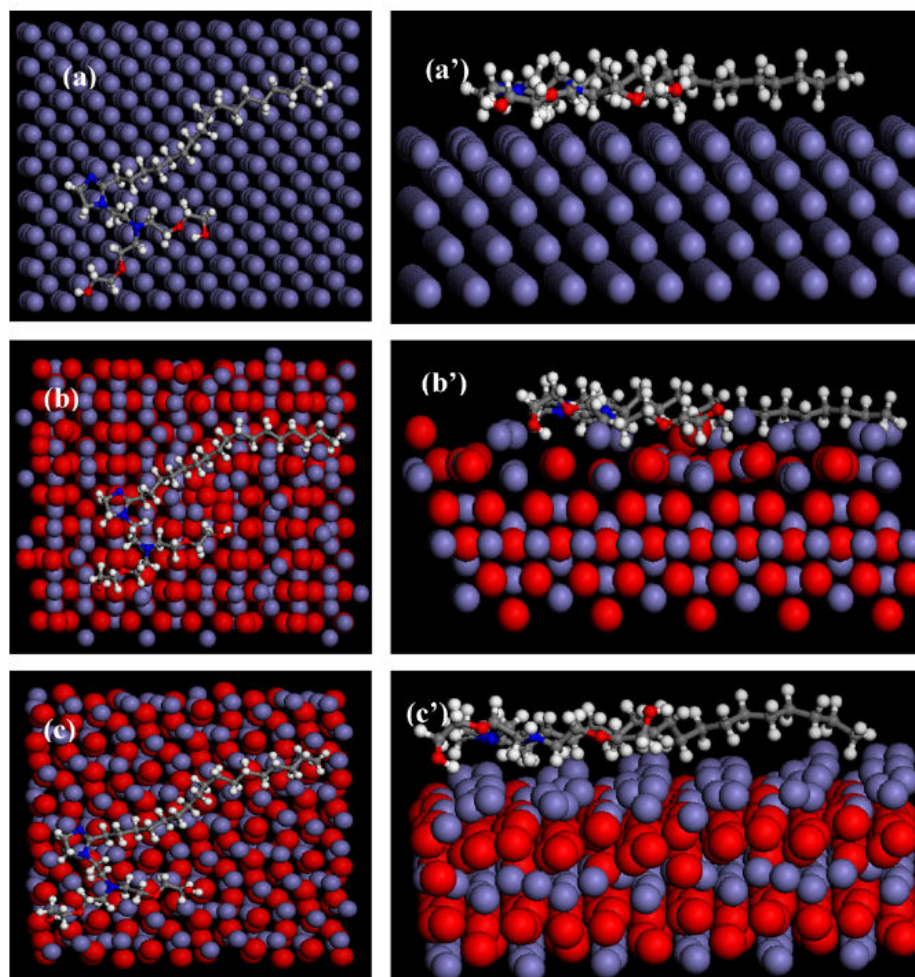


Figure 10. Equilibrium adsorption of HASI on (a) Fe, (b) Fe_3O_4 and (c) Fe_2O_3 surfaces. The left is top view and the right is side view [Adapted from ref. [37]].

6. Future developments

Density functional theory (DFT) has become an attractive theoretical method, because it gives exact, basic, and vital parameters for small and even complex molecules at lower cost. Moreover by applying DFT methodology, we can understand reactivity behaviour in terms of hard and soft acid/base (HSAB) theory that provides a systematic way for analyzing and predicting inhibitor/surface interaction. However, it has been observed that it is difficult to acquire information about the actual interaction and binding strength between organic inhibitor and metal surface which is pertinent in estimating inhibitor performance.

The above deficiency of DFT can be solved by using molecular dynamic simulations, which in recent times have been used to study the interaction between corrosion inhibitors and metal surfaces. MD simulations gives information at the molecular level on the adsorption of the inhibitor molecules on corroding metal surfaces. Furthermore, vital information on the conformation of inhibitors adsorbed onto metal surfaces and the interaction energy between them can be readily obtained [45]. Thus, MD simulations methodology can provide powerful insights into the design of inhibitor systems with superior properties and differences in inhibition efficiency among homologues inhibitors (inhibitors bearing similar structures) can be systematically explained. Furthermore, the use of molecular dynamic simulations in conjunction with DFT, will model completely the complex interaction involved in corrosion inhibition process of carbon steel (for example, the adsorption of water, electrolyte anion and the inhibitor onto the metal surface (Fig. 11) [46]. This will help in the calculation of parameters like adsorption and binding energies of the organic inhibitor materials, the electrolyte anion and water onto the metal surface.

Another important consideration in the future design of organic corrosion inhibitor will be to modeled the interaction between the inhibitor molecule and the metal oxide layer using DFT in conjunction with the molecular dynamic simulations approach. During the corrosion of mild steel in aqueous CO₂ environments, FeCO₃, Fe₃O₄ and Fe₂O₃ have be found in corrosion product films [47]. It should be noted that the process of metal corrosion is complex and heterogeneous due to the presence of various anodic and cathodic sites on the metal surface. For FeCO₃ surface, cation Fe²⁺ is present as anodic reactive site, which can bind to electrophilic attacking centers in inhibitors molecules. Anion CO₃²⁻ is present as a cathodic reactive center, which can bind to nucleophilic centers in inhibitor molecules. Therefore, inhibitor molecule can be adsorbed onto the FeCO₃ surface through interaction with these sites, and as a result, the transport of corrosive species is restricted from solution to metal surface. Thus, electrochemical reactions are retarded. The result of the molecular dynamic simulations calculation will enable the determination of the binding energy, which is an important factor to characterize the adsorption ability of an inhibitor molecule onto the FeCO₃ surface (Figs. 12 and 13) [48]. The binding energies will enable us to predict the most efficient inhibitors from a family of organic compounds with related structures.

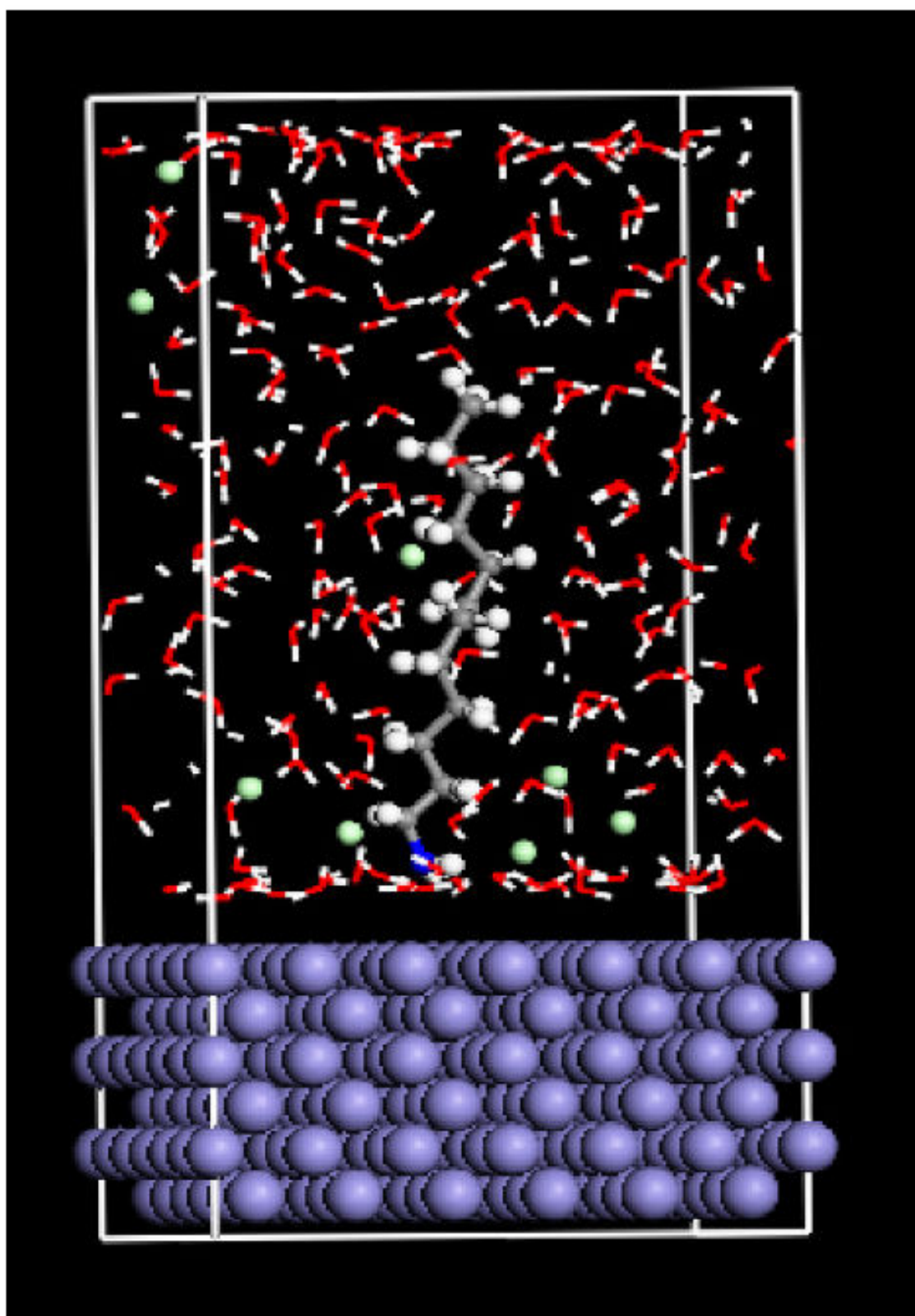


Figure 11. Equilibrium configuration of dodecylamine in aqueous solutions containing chloride ions [46].

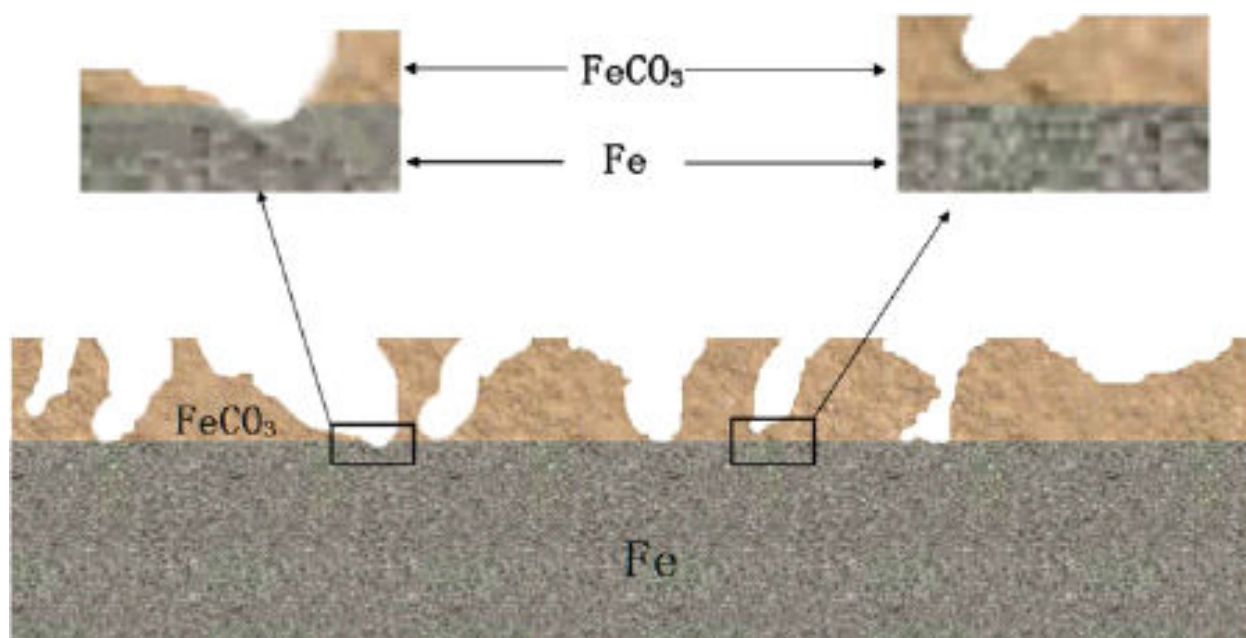


Figure 12. Sketch of corroded Fe surface in CO_2 containing environment [48].

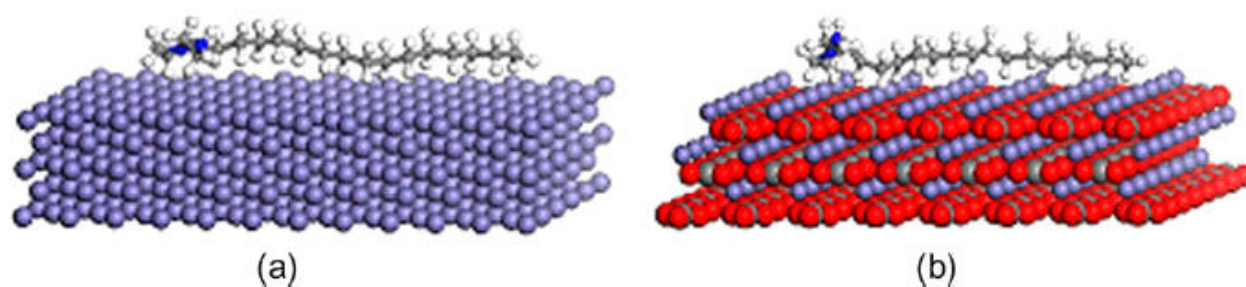


Figure 13. Equilibrium adsorption configuration of inhibitor 1-(2-aminoethyl)-2-alkyl-imidazoline derivative on (a) Fe and FeCO_3 (b) surfaces [48].

Finally, An important future consideration in the design of new and effective corrosion inhibitors using DFT will be to identify organic structures that have low toxicity in addition to having high corrosion protection efficiencies. In this regard, LogS, LogP, dipole moment and quantum chemical descriptors which are often used to model toxicities of therapeutic drugs could also be used for organic corrosion inhibitors since there are many similarities between the properties of drugs and the properties of corrosion inhibitors. For both applications (drugs and corrosion inhibitors), the organics need to have some solubility in water (Log S) and also a certain level of lipophilicity (Log P) (i.e. partitioning into the fatty tissues compared to partitioning from water to the metal surface).

7. Conclusion

This chapter has focused on describing the use of modern quantum chemical methods, primarily in the form of Density Functional Theory as a tool in the design of organic materials for the protection of metals in aqueous solution. It is evident that DFT is a powerful technique with a unique capability of performing practical calculations on complex, many bodied systems, such as large organic molecules of which most inhibitors comprise. DFT offers the facility to design, at the molecular level, the molecular structure, including the choice and location of various functional groups and to build in selected aromaticity, as dictated by experimental feedback from studies on existing inhibitors. The use of DFT in conjunction with molecular dynamic simulations, will model completely the complex interaction involved in corrosion inhibition process of carbon steel (for example, the adsorption of water, electrolyte anion and the inhibitor onto the metal surface and also the state of the metal surface whether it is bare or oxide covered.

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