May-July.2012, Vol.2.No.3, 1151-1165. e- ISSN: 2249 –1929

Journal of Chemical, Biological and Physical Sciences

An International Peer Review E-3 Journal of Sciences

Available online at www.jcbsc.org

Section A: Chemical Sciences

CODEN (USA): JCBPAT

Research Article

Theoretical evaluation on the efficiencies of some Flavonoids as corrosion inhibitors on Copper

P.Udhayakala[1]*, T.V. Rajendiran[2] and S. Gunasekaran[3]

[1] Department of Chemistry, Dr.MGR Educational and Research Institute, Chennai -600095, India

[2] Department of Chemistry, Pachaiyappa's College, Chennai - 600 030, India

[3]Department of Physics, Spectrophysics Research Laboratory, Pachaiyappa's College, Chennai- 600 030, India

Received: 8 April 2012; Revised: 30 April 2012; Accepted: 10 May 2012

ABSTRACT

Corrosion inhibition performance of three flavonoids , ie., apigenin (C1), luteolin-3'-methyl ether (C2) and quercetin-3,3'-dimethylether (C3) on copper was evaluated by density functional theory (DFT) at the B3LYP/6-31G(d,p) level. Quantum chemical parameters most relevant to their potential action as corrosion inhibitors, such as E_{HOMO}, E_{LUMO}, the energy gap(ΔE), hardness(η), Softness(S), dipole moment(μ), electron affinity(EA), ionization potential(IE), the absolute electronegativity (χ) , the fraction of electron transferred (ΔN), electrophilicity index(ω) and the back-donation($\Delta E_{Back\text{-}donation}$) have been calculated. The local reactivity has been analysed through the Fukui and condensed softness indices in order to predict both the reactive centres and to know the possible sites of nucleophilic and electrophilic attacks. The theoretical conclusions were found to be consistent with the experimental data reported.

Keywords: Flavonoids , quantum chemical descriptors, reactivity, DFT, Fukui function, softness indices, electrophilicity index.

INTRODUCTION

Copper is one of the most important material used widely in different industries, especially in central heating installations, oil refiners, energetic and marine environment because of its excellent conductivity, good mechanical workability and relatively low cost and reactivity. It is relatively a noble metal;

however, it is susceptible to corrosion by acids and strong alkaline solutions. The use of inhibitors is one of the most practical methods for protecting metals or alloys from corrosion. Inhibitors are chemicals that often work by adsorbing themselves on the metallic surface by forming a film [1-3]. Organic compounds containing polar groups including nitrogen, sulfur, and oxygen [4-8], and heterocyclic compounds with polar functional groups and conjugated double bonds [9-11] have been reported to inhibit copper corrosion. The inhibiting action of these organic compounds is usually attributed to their interactions with the copper surface via their adsorption. Even though many synthetic organic compounds showed good anticorrosive activity, most of them are highly toxic to both human beings and the environment. Presently, many researchers have reoriented their studies to the use of naturally occurring substances. Naturally occurring substances are cheap and renewable, biodegradable and do not contain heavy metals or other toxic chemicals and are therefore eco-friendly and hence ecologically acceptable.

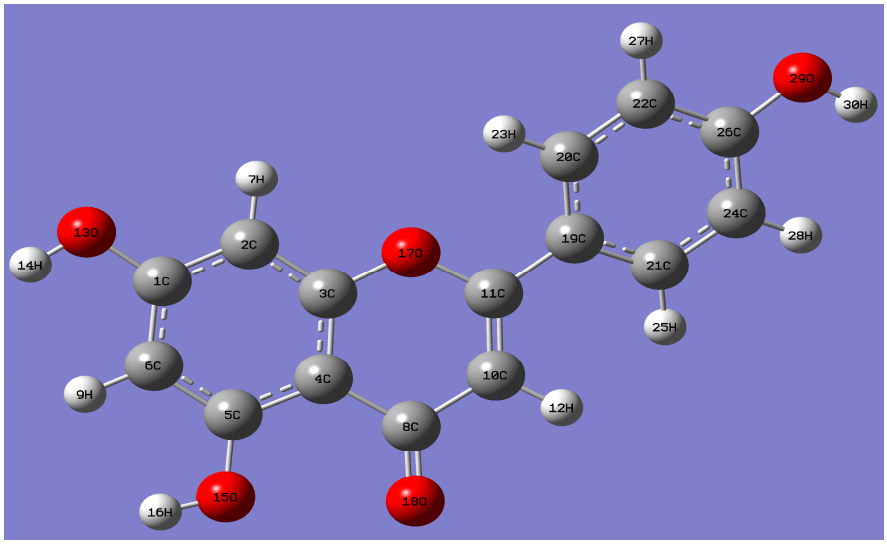
The Flavonoids, one of the most numerous and wide spread groups of natural secondary constituents, important to man not only because they contribute to plant color but also many members are physiologically active [12]. Flavonoids have antioxidant activity, anti-allergic, anti-cancer, anti-inflammatory and anti-viral[13]. Nelly N. Mateeva *et al.* have reported the synthesis of novel flavonoid derivatives as potential HIV- Integrase inhibitors[14]. Theoretical study of the structural and electronic properties of luteolin and apigenin dyes were reported by Anna Amat *et al.*[15]. The objective of the present paper is to extend the study of Mahmoud A. Al-Qudah [16] by analyzing the inhibitive properties of three flavonoids , ie., apigenin(C1), luteolin-3'-methylether (C2) and quercetin-3,3'-dimethylether (C3) by Density Functional Theory (DFT) calculations. Results obtained showed that the inhibition efficiency is in the order of C3>C2>C1. It is well correlated with the experimental results. From the calculations we have explained which adsorption site is favoured to bind to the metal surface. The local reactivity has been analyzed by means of the Fukui indices, since they indicate the reactive regions, in the form of the nucleophilic and electrophilic behavior of each atom in the molecule.

Quantum chemistry calculations have been widely used to evaluate the inhibition efficiency of corrosion inhibitors among all computer simulation methods. The reactive ability of the inhibitor is closely linked to their frontier molecular orbital (FMO). Quantum chemical studies have been successfully performed to link the corrosion inhibition efficiency with molecular orbital (MO) energy levels for some kinds of organic compounds[17,18]. With this method, the capability of inhibitor molecules to donate or accept electrons can be predicted with analysis of global reactivity parameters such as E_{HOMO}, E_{LUMO}, energy gap (ΔE), the dipole moment, electronegativity (χ), global hardness (η), softness, electrophilicity index and the fraction of electrons transferred from the inhibitor molecule to the metallic atom (ΔN) and the back-donation($\Delta E_{\text{Back-donation}}$).

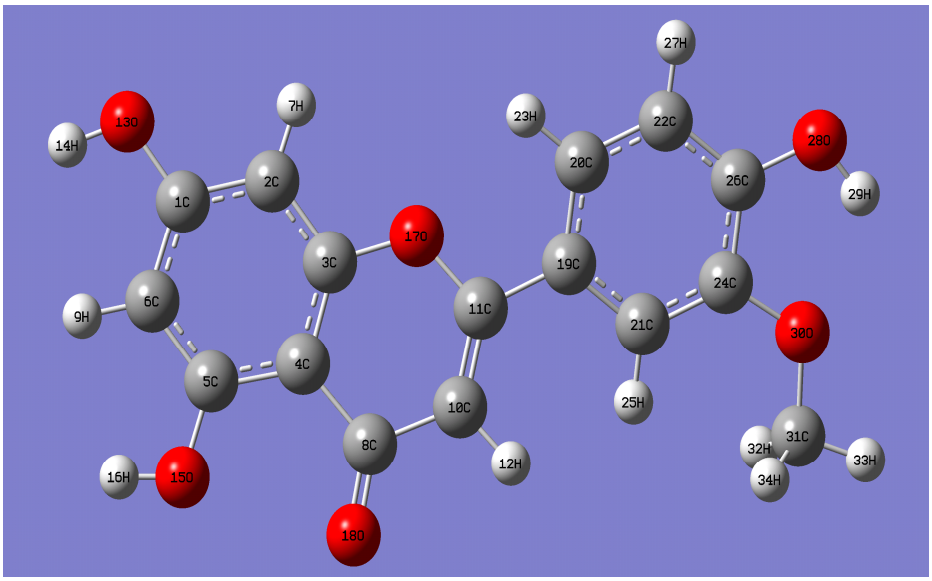
MATERIALS AND METHODS

Quantum-chemical calculations methodology: Among quantum chemical methods for evaluation of corrosion inhibitors, density functional theory (DFT) has shown significant promise[19] and appears to be adequate for pointing out the changes in electronic structure responsible for inhibitory action. In order to explore the theoretical-experimental consistency, quantum chemical calculations were performed with complete geometry optimizations using standard Gaussian-03 software package[20]. Geometry optimization were carried out by B3LYP functional at the 6-31G (d,p) basis set [21].

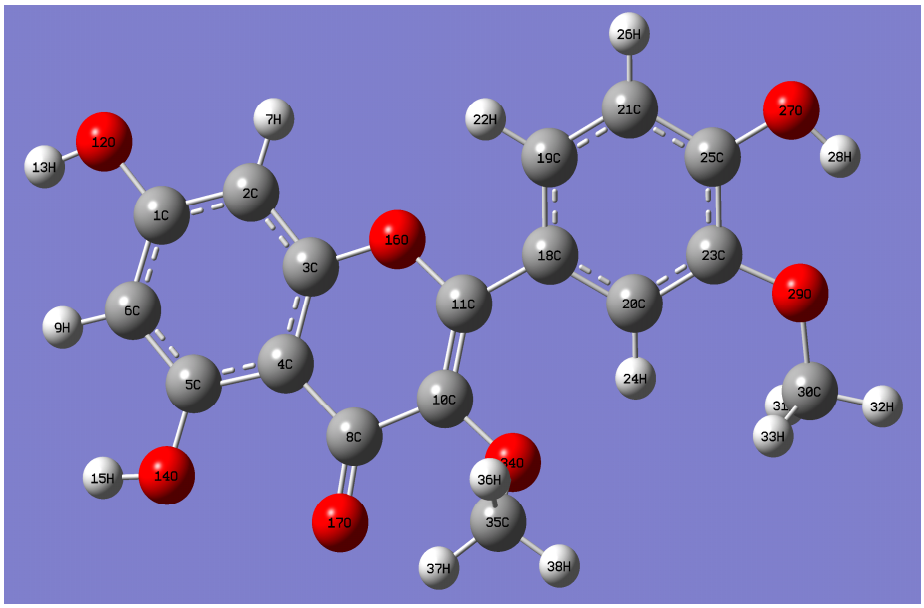
This basis set provided accurate geometry and electronic properties of a wide range of organic compounds[22]. Recently, Density functional theory (DFT) has been used to analyze the characteristics of the inhibitor/ surface mechanism and to describe the structural nature of the inhibitor in the corrosion process[23,24]. Furthermore, DFT is considered a very useful technique to probe the inhibitor/surface interaction as well as to analyze the experimental data. The results of the geometry optimization of the compounds C1, C2 and C3 are presented in **Figure 1.**



apigenin(C1)



luteolin-3’-methylether (C2)



quercetin-3,3’-dimethylether (C3)

Figure 1: Optimized molecular structure of C1, C2, and C3 by B3LYP/6-31G(d,p)

RESULTS AND DISCUSSION

Density functional theory (DFT) has become an attractive theoretical method because it gives exact basic vital parameters for even huge complex molecules at low cost [25,26]. It has been quite successful in providing theoretical basis for popular qualitative chemical concepts like electronegativity (χ), hardness (η), softness(S) and local ones such as Fukui function, F(r) and local softness, s(r). The basic relationship of the density functional theory of chemical reactivity is precisely, the one established by Parr, Donnelly, Levy and Palke[27], that links the chemical potential of DFT with the first derivative of the energy with respect to the number of electrons, and therefore with the negative of the electronegativity χ.

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{v(r)} = -\chi$$

Where μ is the electronic chemical potential, E is the total energy, N is the number of electrons, and ν(r) is the external potential of the system.

Hardness (η) has been defined within the DFT as the second derivative of the total energy with respect to N at $v(r)$ property which measures both the stability and reactivity of the molecule [28].

$$\eta = \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r)}$$

In this formula, N is the number of electrons, $v(r)$ is the external potential due to nuclei and μ is the electronic chemical potentials.

According to Koopman's theorem [29] the ionization potential (I) and electron affinity (A) are related to E_{HOMO} and E_{LUMO} by the following equation.

$$I = -E_{HOMO}$$

$$A = -E_{LUMO}$$

These quantities are related to the electronegativity(χ) and the global hardness(η) of the molecule using the following relations[30].

$$\chi = \frac{I+A}{2}$$

$$\eta = \frac{I-A}{2}$$

The global softness(S) is the inverse of the global hardness[31].

$$S = \frac{1}{\eta} = \frac{2}{I-A}$$

In the chemical reactivity theory, the parameters like electronegativity, hardness and softness have proved to be very useful quantities. The electronegativity of the inhibitor molecules are lower than the bulk copper. Hence, electron move from the molecules with lower electronegativity (inhibitor compound) toward that of a higher value (metal surface) until the equilibrium in chemical potential is reached.

The global electrophilicity index (ω), introduced by Parr[32], calculated using the electronic chemical potential and chemical hardness is given by

$$\omega = \frac{\mu^2}{2\eta}$$

According to the definition, this index measures the propensity of chemical species to accept electrons[33]. A good, more reactive, nucleophile is characterized by lower value of ω; and conversely a good electrophile is characterized by a high value of ω. This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge ΔN from the environment.

According to Pearson theory[30] the fraction of transferred electrons (ΔN) from the inhibitor molecule to the metallic atom can be calculated. For a reaction of two systems with different electronegativities (as a metallic surface and an inhibitor molecule) the following mechanism will take place: the electronic flow will occur from the molecule with the lower electronegativity towards that of higher value, until the chemical potentials are the same. For the calculation the following formula was used[30].

$$\Delta N = \frac{\chi_{cu} - \chi_{inh}}{\left[2(\eta_{cu} + \eta_{inh}\right]}$$

Where χ_{Cu} and χ_{inh} denote the absolute electronegativity of copper and inhibitor molecule respectively η_{Cu} and η_{inh} denote the absolute hardness of copper and the inhibitor molecule respectively. In order to calculate the fraction of electrons transferred, the theoretical value for the electronegativity of bulk copper was used χ_{Cu}=4.98 eV [34] and a global hardness of η_{Cu}= 0 by assuming that for a metallic bulk I= A[35] because they are softer than the neutral metallic atoms.

The local selectivity of a corrosion inhibitor is best analyzed by means of condensed Fukui function. The change in electron density is the nucleophilic $f^+(r)$ and electrophilic $f^-(r)$ Fukui functions, which can be calculated using the finite difference approximation as follows [36].

$$f_k^+ = q_{N+1} - q_N$$

$$f_k^- = q_N - q_{N-1}$$

where q_N, q_{N+1} and q_{N-1} are the electronic population of the atom k in neutral, anionic and cationic systems.

Condensed softness indices allowing the comparison of reactivity between similar atoms of different molecules can be calculated easily starting from the relation between the Fukui function $f(r)$ and the local softness $s(r)$ [37].

$$s(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)} \left(\frac{\partial N}{\partial \mu}\right)_{v(r)} = f(r)S$$

From this relation, one can infer that local softness and Fukui function are closely related, and they should play an important role in the field of chemical reactivity.

According to the simple charge transfer model for donation and back-donation of charges proposed recently by Gomez *et al.*, [38] an electronic back-donation process might be occurring governing the interaction between the inhibitor molecule and the metal surface. The concept establishes that if both processes occur, namely charge transfer to the molecule and back-donation from the molecule, the energy change is directly proportional to the hardness of the molecule, as indicated in the following expression.

$$\Delta E_{\text{Back-donation}} = -\frac{\eta}{4}$$

The $\Delta E_{Back\text{-}donation}$ implies that when $\eta > 0$ and $\Delta E_{Back\text{-}donation} < 0$ the charge transfer to a molecule, followed by a back-donation from the molecule, is energetically favored. In this context, hence, it is possible to

compare the stabilization among inhibiting molecules, since there will be an interaction with the same metal, then, it is expected that it will decrease as the hardness increases.

Theoretical assessment: According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between frontier orbital (HOMO and LUMO) of reacting species[39]. Thus, the treatment of the frontier molecular orbital separately from the other orbital based on the general principles governing the nature of chemical reactions, the energy of the highest occupied molecular orbital (E_{HOMO}) measures the tendency towards the donation of electron by a molecule [40]. Increasing values of E_{HOMO} facilitate adsorption and therefore enhance the inhibition efficiency, by influencing the transport process through the adsorbed layer. E_{LUMO} indicates the ability of the molecule to accept electrons. The binding ability of the inhibitor to the metal surface increases with increasing of the HOMO and decreasing of the LUMO energy values. The frontier molecular orbital diagrams of C1, C2 and C3 are represented in figure 2. Table 1 represents the total energy and calculated energy levels of the HOMO, LUMO and energy gap in(eV) and dipole moment of the investigated molecules.

Table-1: Global chemical reactivity indices for C1,C2 and C3 calculated using B3LYP/6-31G(d,p).

Parameters	C1	C2	C3
E (au)	-953.74166	-1068.26873	-1182.78554
E_{HOMO}(eV)	-5.8262	-5.6553	-5.3885
E_{LUMO} (eV)	-1.3717	-1.3489	-1.3355
Energy gap(ΔE) (eV)	4.4545	4.3064	4.053
Dipole moment(μ)D	2.4234	1.3592	1.7404

E_{HOMO} is a quantum chemical parameter which is often associated with the electron donating ability of the molecule. High value of E_{HOMO} is likely to a tendency of the molecule to donate electrons to appropriate acceptor molecule of low energy empty molecular orbital[41]. The inhibitor does not only donate electron to the unoccupied d orbital of the metal ion but can also accept electron from the d-orbital of the metal leading to the formation of a feedback bond. From Table 1, it can be clearly seen that the highest value of E_{HOMO} -5.3885 (eV) of C3 indicates the better inhibition efficiency. This is in agreement with the experimentally determined inhibition efficiencies.

The energy gap, ($\Delta E = E_{LUMO} - E_{HOMO}$) is an important parameter as a function of reactivity of the inhibitor molecule towards the adsorption on the metallic surface. As ΔE decreases the reactivity of the molecule increases leading to increase in the inhibition efficiency of the molecule[42]. Lower values of the energy difference will render good inhibition efficiency, because the energy to remove an electron from the last occupied orbital will be low[43]. A molecule with a low energy gap is more polarizable and is generally associated with the high chemical activity and low kinetic stability and is termed soft molecule[44]. Soft molecule is more reactive than a hard molecule because a hard molecule has a large energy gap. The results as indicated in table1 shows that inhibitor C3 has the lowest energy gap, this means that the molecule could have better performance as corrosion inhibitor.

The dipole moment (μ) is another parameter of the electronic distribution in a molecule and is the measure of polarity of a polar covalent bond. In our case, the order of dipole moment is not correlated with the

experimental results. Literature survey reveals that several irregularities appeared in case of correlation of dipole moment with inhibitor efficiency[45]. In general, there is no significant relationship between the dipole moment values and inhibition efficiencies[46].

Table-2: Quantum chemical descriptors for inhibitor C1, C2 and C3 calculated using B3LYP/6-31G(d,p).

Parameters	C1	C2	C3
Ionization potential (I) /(eV)	5.8262	5.6553	5.3885
Electron affinity (A) /(eV)	1.3717	1.3489	1.3355
Chemical Potential (μ) /eV	-3.59895	-3.50195	-3.3619
Global Hardness(η) / eV	2.22725	2.1532	2.02645
Electronegativity(χ) (eV	3.59895	3.50195	3.36195
Global softness(S)	0.44898	0.46443	0.49347
Electrophilicity (ω)	2.90772	2.8477	2.7887

Ionization energy is a fundamental descriptor of the chemical reactivity of atoms and molecules. High ionization energy indicates high stability and chemical inertness and small ionization energy indicates high reactivity of the atoms and molecules[47]. The low ionization energy 5.3885 (eV) of C3 indicates the high inhibition efficiency.

Absolute hardness and softness are important properties to measure the molecular stability and reactivity. It is apparent that the chemical hardness fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has a large energy gap and a soft molecule has a small energy gap[48]. In our present study C3 has low hardness value 2.02645 (eV) compared with the other molecules C1 and C2. Normally, the inhibitor with the least value of global hardness (hence the highest value of global softness) is expected to have the highest inhibition efficiency[49]. For the simplest transfer of electron, adsorption could occur at the part of the molecule where softness(S), which is a local property, has a highest value[50]. In our case, the molecule C3 with the softness value of 0.49347 has the highest inhibition efficiency.

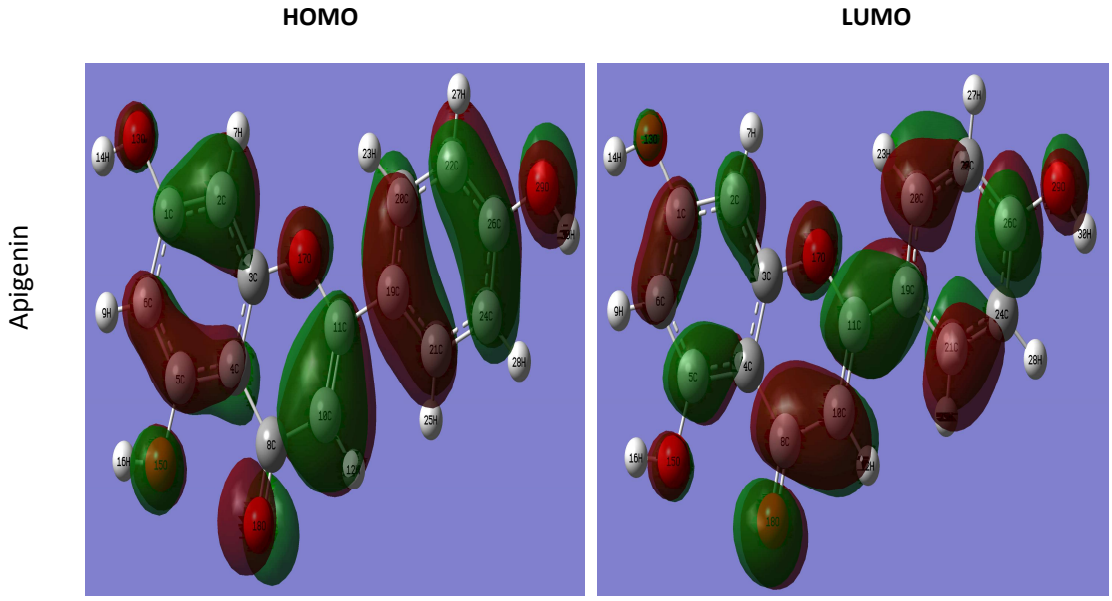
The absolute electronegativity is the chemical property that describes the ability of a molecule to attract electrons towards itself in a covalent bond. According to Sanderson's electronegativity equalization principle[51], the molecule C1 with a high electronegativity quickly reaches equalization and hence low reactivity is expected which in turn indicates low inhibition efficiency. The table 2 shows the order of electronegativity as C1> C2> C3. Hence an increase in the difference of electronegativity between the metal and the inhibitor is observed in the order C3> C2> C1. The electrophilicity index, ω, shows the ability of the inhibitor molecules to accept electrons. It is a measure of the stabilization in energy after a system accepts additional amount of electron charge from the environment[52]. In our present study, C3 is the strongest nucleophile while C1 is the strongest electrophile.

The number of electrons transferred (Δ*N*) was also calculated and tabulated in Table 3. Values of Δ*N* show that the inhibition efficiency resulting from electron donation agrees with Lukovits's study[33]. If Δ*N* < 3.6, the inhibition efficiency increases by increasing electron-donating ability of these inhibitors to

donate electrons to the metal surface and it increases in the following order: C3> C2> C1. The results indicate that ΔN values correlates strongly with experimental inhibition efficiencies. Thus, the highest fraction of electrons transferred is associated with the best inhibitor (C3), while the least fraction is associated with the inhibitor that has the least inhibition efficiency (C1).In **Table 3**, the calculated $\Delta E_{back\text{-}donation}$ values for the inhibitors are listed. The order followed is: C3> C2> C1, which indicates that back-donation, is favoured for the C3, which is the best inhibitor.

Table -3: The number of electron transferred (ΔN) and ΔE back donation (eV) calculated for inhibitor C1, C2 and C3.

Parameters	C1	C2	C3
Transferred electrons fraction (ΔN)	0.31003	0.34322	0.39924
ΔE back-donation / (eV)	-0.55681	-0.53831	-0.50661



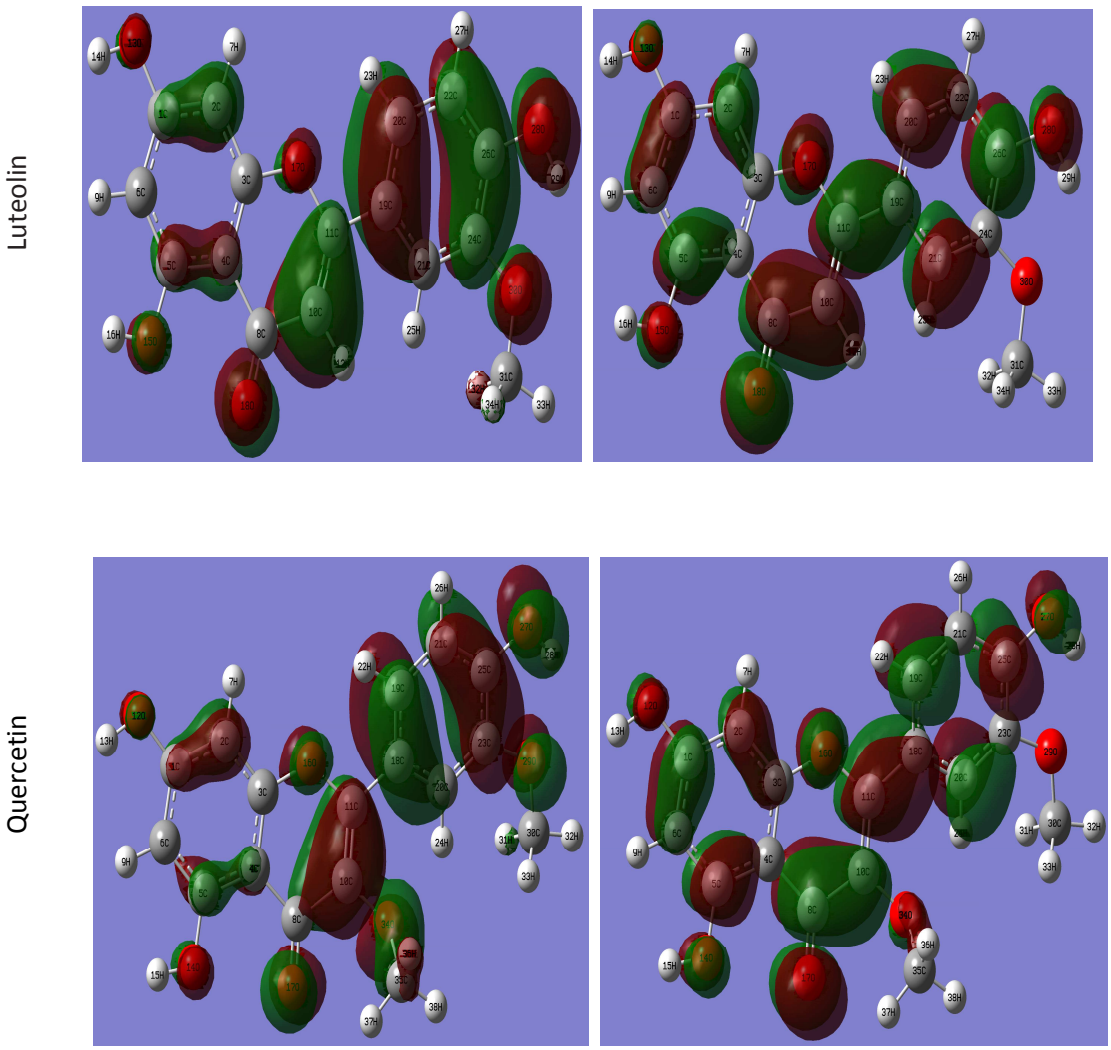


Figure-2: Frontier molecular orbital diagrams of C1, C2 and C3 by B3LYP/6-31G(d,p)

The use of Mulliken population analysis to estimate the adsorption centres of inhibitors has been widely reported and it is mostly used for the calculation of the charge distribution over the whole skeleton of the molecule[53]. There is a general consensus by several authors that the more negatively charged heteroatom, is the more it can be adsorbed on the metal surface through the donor-acceptor type reaction[54]. It is important to consider the situation corresponding to a molecule that is going to receive a certain amount of charge at some centre and is going to back donate a certain amount of charge through the same centre or another one[38] . Parr and Yang proposed that larger value of Fukui function indicate more reactivity[17]. Hence greater the value of condensed Fukui function, the more reactive is the particular atomic centre in the molecule.

The local reactivity of molecule C1, C2 and C3 is analyzed by means of the condensed Fukui function. The condensed Fukui function and local softness indices allow one distinguish each part of the molecule on the basis of its distinct chemical behaviour[55] due to the different substituted functional group. The f_k^+ ,measures the changes of density when the molecules gains electrons and it corresponds to reactivity with respect to nucleophilic attack. On the other hand, f_k^- corresponds to reactivity with respect to electrophilic attack or when the molecule loss electrons. For electrophilic attack the most reactive site of molecule C1 is on the O(29) atom and for nucleophilic attack the most reactive site is the O(18) atom. In the molecule C2 the most reactive site for electrophilic attack is in atom O(28) and favourable nucleophilic attack is in atom O(18). In the molecule C3, the electrophilic attack site is in atom C(10) and nucleophilic attack takes place in atom O(17). The electrophilic and nucleophilic attacks of molecule C1, C2 and C3 are tabulated in **Table 4, 5 and 6**.

Table- 4: Fukui and local softness indices for electrophilic and nucleophilic attacks in C1 atoms calculated from Mulliken atomic charges.

Atom	f^-	f^+	s_k^-	s_k^+
1C	0.01490	0.01851	0.00669	0.00831
2C	0.02931	0.01941	0.01316	0.00871
3C	-0.00085	-0.00839	-0.00038	-0.00377
4C	0.01217	-0.00005	0.00546	-3.63674
5C	0.02727	0.04109	0.01224	0.01845
6C	0.02672	0.01920	0.01199	0.00862
7H	0.04486	0.03877	0.02014	0.01741
8C	0.01266	0.03735	0.00568	0.01677
9H	0.05007	0.04977	0.02248	0.02234
10C	0.06710	0.02519	0.03012	0.01130
11C	0.03540	0.07075	0.01589	0.03176
12H	0.05859	0.06067	0.02630	0.02724
13O	0.03789	0.02959	0.01701	0.01328
14H	0.02460	0.02117	0.01104	0.00950
15O	0.03660	0.01511	0.01643	0.00678
16H	0.02937	0.02737	0.01318	0.01228
17O	0.01949	0.02580	0.00875	0.01158
18O	0.05979	**0.10587**	0.02684	**0.04753**
19C	-0.00318	0.00420	-0.00142	0.00188
20C	0.02775	0.03277	0.01246	0.01471
21C	0.02648	0.02956	0.01189	0.01327
22C	0.01991	0.00213	0.00894	0.00095
23H	0.03988	0.04384	0.01790	0.01968
24C	0.01675	0.00092	0.00752	0.00041
25H	0.03889	0.04495	0.01746	0.02018
26C	0.03140	0.05566	0.01410	0.02499
27H	0.05650	0.05816	0.02537	0.02611
28H	0.05634	0.05819	0.02529	0.02612
29O	**0.06928**	0.04525	**0.03110**	0.02031
30H	0.03393	0.02711	0.01523	0.01217

Table- 5: Fukui and local softness indices for electrophilic and nucleophilic and attacks in C2 atoms calculated from Mulliken atomic charges.

Atom	f^-	f^+	s_k^-	s_k^+
1C	0.01357	0.01808	0.00630	0.00839
2C	0.02038	0.01913	0.00946	0.00888
3C	0.00049	-0.00836	0.00023	-0.00388
4C	0.00966	-0.00006	0.00448	-3.06524
5C	0.02471	0.04031	0.01147	0.01872
6C	0.02202	0.01893	0.01023	0.00879
7H	0.03524	0.03819	0.01636	0.01774
8C	0.01044	0.03733	0.00485	0.01734
9H	0.04411	0.04891	0.02048	0.02271
10C	0.06211	0.02345	0.02884	0.01089
11C	0.03211	0.07040	0.01491	0.03269
12H	0.05079	0.05927	0.02359	0.02753
13O	0.03352	0.02912	0.01556	0.01352
14H	0.02190	0.02080	0.01017	0.00966
15O	0.02859	0.01471	0.01328	0.00683
16H	0.02556	0.02686	0.01187	0.01247
17O	0.00689	0.02583	0.00320	0.01199
18O	0.05385	**0.10349**	0.02501	**0.04806**
19C	0.00222	0.00443	0.00103	0.00205
20C	0.03425	0.03047	0.01590	0.01415
21C	0.02369	0.03835	0.01100	0.01781
22C	0.02510	0.00046	0.01165	0.00021
23H	0.04926	0.04309	0.02287	0.02001
24C	0.03468	0.01413	0.01610	0.00656
25H	0.03180	0.03518	0.01477	0.01634
26C	0.03720	0.06051	0.01727	0.02810
27H	0.05982	0.05598	0.02778	0.02600
28O	**0.08372**	0.04753	**0.03888**	0.02207
29H	0.03216	0.02332	0.01494	0.01083
30O	0.02266	0.01274	0.01052	0.00591
31C	-0.02670	-0.02319	-0.01240	-0.01077
32H	0.02606	0.01546	0.01210	0.00718
33H	0.04172	0.04010	0.01937	0.01862
34H	0.02624	0.01491	0.01218	0.00692

Table- 6: Fukui and local softness indices for electrophilic and nucleophilic attacks in C3 atoms calculated from Mulliken atomic charges.

Atom	f^-	f^+	s_k^-	s_k^+
1C	0.01379	0.02139	0.00680	0.01055
2C	0.01418	0.01925	0.00700	0.00950
3C	0.00029	-0.00456	0.00014	-0.00225
4C	0.00364	-0.01154	0.00179	-0.00569
5C	0.02304	0.04624	0.01137	0.02282
6C	0.01907	0.01574	0.00941	0.00776
7H	0.03063	0.03927	0.01511	0.01938
8C	0.00293	0.05564	0.00144	0.02745
9H	0.04045	0.04922	0.01996	0.02429
10C	**0.08550**	0.04469	**0.04219**	0.02205
11C	0.04144	0.04845	0.02045	0.02391
12O	0.02967	0.03045	0.01464	0.01502
13H	0.01982	0.02126	0.00978	0.01049
14O	0.01519	0.01573	0.00749	0.00776
15H	0.02253	0.02741	0.01112	0.01352
16O	0.01445	0.02991	0.00713	0.01476
17O	0.04185	**0.10789**	0.02065	**0.05324**
18C	-0.00282	0.00447	-0.0014	0.00220
19C	0.03148	0.02963	0.01553	0.01462
20C	0.02342	0.04196	0.01156	0.02070
21C	0.01926	0.00011	0.00950	0.00005
22H	0.04369	0.03541	0.02156	0.01747
23C	0.03095	0.01287	0.01527	0.00635
24H	0.01169	0.02822	0.00577	0.01393
25C	0.03372	0.05197	0.01664	0.02564
26H	0.05333	0.05125	0.02631	0.02529
27O	0.06967	0.04399	0.03438	0.02170
28H	0.02736	0.02123	0.01350	0.01047
29O	0.01829	0.01202	0.00902	0.00593
30C	-0.02044	-0.01992	-0.0101	-0.00983
31H	0.01623	0.01168	0.00800	0.00576
32H	0.03880	0.03784	0.01915	0.01867
33H	0.01563	0.01238	0.00772	0.00610
34O	0.04323	0.00385	0.02133	0.00190
35C	0.00110	-0.02644	0.00054	-0.01304
36H	0.07163	0.03035	0.03534	0.01497
37H	0.02591	0.01465	0.01278	0.00723
38H	0.02926	0.04590	0.01444	0.02265

CONCLUSION

The corrosion inhibition efficiencies of three flavonoid compounds was investigated using density functional theory at B3LYP/6-31-G(d,p) basis set. Quantum chemical parameters such as E_{HOMO}, E_{LUMO}, energy gap(ΔE), hardness(η), Softness(S), electron affinity(EA), ionization potential(IE), the absolute electronegativity (χ) , the fraction of electron transferred (ΔN), electrophilicity index(ω) and the back-donation($\Delta E_{Back\text{-}donation}$) were calculated The inhibition efficiency of the molecules C1,C2 and C3 obtained quantum chemically increase with the increase in E_{HOMO}, and decrease in energy gap (ΔE). C3 has the highest inhibition efficiency because it had the highest HOMO energy and ΔN values and lowest energy gap it was most capable of offering electrons and it could have a better performance as corrosion inhibitor. Fukui function shows the nucleophilic and electrophilic attacking sites in the investigated inhibitors. The Comparison of theoretical and experimental data exhibit good correlation confirming the reliability of the method employed here.

REFERENCES

1. E.A. Noor, *J Eng. Appl. Sci.*, 2008, **3(1),** 23.

2. E.E. Ebenso, N.O. Eddy, A.O. Odongenyi, *Afri. J. Pure Appl. Chem*., 2008, **4(11),** 107.

3. E.E. Oguzie, *Pigment Resin Technol.*, 2006, **35(6),**334.

4. H. Otmacic, J. Telegdi, K. Papp, E. Stupnisek-Lisac, *J. Appl. Electrochem.*, 2004,**34** , 545.

5. H. Ma, S. Chen, L. Niu, S. Zhao, S. Li, D. Li, *J. Appl. Electrochem*., 2002,**32** , 65

6. C. Wang, S. Chen, S. Zhao, *J. Electrochem. Soc.*, 2004, **151,** B11.

7. M. Kendig, S. Jeanjaquet, *J. Electrochem. Soc*., 2002, **149,** B47.

8. H.Y. Ma, C. Yang, B.S. Yin, G.Y. Li, S.H. Chen, J.L. Luo, *J. Appl.Surf. Sci*, 2003, **218,** 143.

9. M.A. Elmorsi, A.M. Hassanein, *Corros. Sci.* 1999, **41** 2337.

10. F.M. Al-Kharafi, *Corros. Sci.* 1988, **28,** 163.

11. M. Scendo, D. Poddebniak, J. Malyszko, *J. Appl. Electrochem.*, 2003, **33,** 287.

12. T.B.Harborne , Pytochemical Methods., Chapman and Hall, New York, 1984.

13. P.K.Agrawal , Carbon-13NMR of flavonoids. Elsevier science publishers, Amsterdam, 1989.

14. Nelly N. Mateeva, Rao N. Kode, Kinfe K. Redda, *J. Heterocyclic. Chem*., 2002,**39**(6), 1251.

15. Anna Amat, Antonio Sgamellotti, Simona Fantacci, *Energy* .,1986,**34(10)**, 1141.

16. Mahmoud A. Al-Qudah, *E-Journal of Chemistry*., 2011, **8(1),** 326.

17. J.Fang and J.Li, J .Mol. Struct. (Theochem), 2002, **593**, 179.

18. T.Arslan, F.Kandemirli, E.E.Ebenso, I. Love and H. Alemu, *Corros. Sci*., 2009, **51**, 35.

19. N. Lopez, F. Illas, *J. Phys., Chem B,* 1998, **102** (8),1430.

20. M.J.Frisch, G.W.Trucks and H.B.Schlegel *et al.* Gaussian 03, Gaussian, Inc.: Pittsburgh PA, (2003).

21. R.G.Parr and W. Yang, Density Functional Theory of Atoms and Molecules; (Oxford University Press: New York, 1989).

22. R.Henriquez, M.Sancy , M.A.Paez , L.Padilla-Campos, J.H. Zaegal, C.M.Rangel, J.Costamagna and G.Gardenas-Jiron., J.*Mol. Struct.* (Theochem)., 2005, **757**, 1.

23. L.Rodriguez-Valdez, A.Martinez-Villafane and D.Glossman- Mitnik, *J.Mol.Struct.*, (Theochem). 2005, **716,** 61.

24. M.Lashkari and M.R. Arshadi., *Chem. Phys*, 2004, **299**, 131.

25. D. Q. Zhang, Q. R. Cai, X. M. He; L. X. Gao, G. S. Kim, *Mat. Chem. Phys*, 2009,**114 (2- 3)**, 612.

26. S. Zor, F. Kandemirli, M. Bingul, *Prot. Met.*, 2009, **45(1)**,46.

27. R.G. Parr, R.A. Donnelly, M. Levy, W.E. Palke, *J. Chem. Phys*., 1978, **68**, 3801.

28. R.G. Parr, R.G. Pearson, *J. Am. Chem. Soc*., 1983,**105**, 7512.

29. T.Koopmans, *Physica.*, 1933**, 1,** 104.

30. R.G.Pearson , *J. Org. Chem.*, 1989, **54**, 1423.

31. A. Lesar, I. Milosev, *Chem. Phys. Lett.*, 2009, **483(4-6)**, 198.

32. R.G.Parr, L.Szentpaly and S.Liu. , *J.Am.Chem.Soc.*, 1999,**121**,1922.

33. I. Lukovits, E. Kalman, F. Zucchi., *Corrosion*, 2001, **57**, 3.

34. H. B. Michaelson, *J. Appl. Phys*., 1977, **48**(11) 4729.

35. M.J.S. Dewar, E. G. Zoebisch, E. F. Heali and J.J.P.Stewart., *J. Am. Chem.* Soc., 1985,**107** (13), 3902.

36. C.Lee, W.Yang and R.G.Parr, *J.Mol.Struct* (Theochem)., 1988,**163**, 305.

37. H.Wang, X.Wang, H.Wang, L.Wang and A. Liu., *J. Mol. Model.*, 2007, **13**, 147

38. B.Gomez, N.V.Likhanova, M.A.Dominguez-Aguilar, R.Martinez-Palou,A.Vela and J.Gasquez, *J.Phy.Chem.*, 2006, **B 110**, 8928.

39. K.Fukui, Theory of Orientation and Stereoselection. Springer-Verlaz, New York. (1975).

40. H.E.El Ashry, A.El Nemr, S.A.Esawy and S.Ragab, *Electrochim. Acta.*, 2006, **51**, 3957.

41 G.Gece and S.Bilgic, *Corros.Sci*. 2009, **51**, 1876 .

42. M. K. Awad, M. R. Mustafa, M. M. Abo Elnga, *J. Mol. Struct. (Theochem)*, 2010, **959,** 66.

43. I.B.Obot, N.O.Obi-Egbedi and S.A.Umoren, *Int.J.Electchem.Sci*., 2009,**4**, 863.

44. I. Fleming, Frontier Orbitals and Organic Chemical Reactions, (John Wiley and Sons, New York, 1976).

45. K. F. Khaled, K. Babic-Samardzija, N. Hackerman, *Electrochim. Acta.*, 2005, **50**, 2515.

46. G. Gece, *Corros. Sci.*, 2008, **50(11)**, 2981.

47. T. Chakraborty and D. C. Ghosh, *Mol. Phys.*, 2010, **108(16)**, 2081.

48. N.O. Obi-Egbedi, I.B. Obot, M.I. El-Khaiary, S.A. Umoren and E.E. Ebenso, *Int. J. Electrochem. Sci*, 2011, **6,** 5649.

49. E.E. Ebenso, D.A. Isabirye, N.O. Eddy, *Int. J. Mol. Sci*., 2010, **11**, 2473

50. R. Hasanov, M. Sadikglu, S. Bilgic, *Appl. Surf. Sci.*, 2007, **253**, 3913

51. P. Geerlings and F. De Proft, *Int. J. Mol. Sci.*, 2002, **3,** 276.

52. S.Liu , *J.Chem.Sci.*, 2005,**117**, 477.

53. M.Sahin, G.Gece, E.Karci and S.Bilgic, *J.Appl.Electrochem.*, 2008, **38**, 809.

54. G.Breket, E.Hur and C.Ogretir, *J.Mol. Struct.*, (THEOCHEM),2002,**578**,79.

55. K.Fukui, T.Yonezewa and H.Shingu, *J.Chem.Phys*., 1952, **20**, 722.

***Correspondence Author: P.Udhayakala;** Department of Chemistry, Dr.MGR Educational and Research Institute, Chennai -600095, India