Journal of Advanced Scientific Research

Available online through http://www.sciensage.info/jasr

ISSN
0976-9595
Research Article

Theoretical Evaluation of Corrosion Inhibition Performance of Some Triazole Derivatives

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ABSTRACT

In this present paper, we have made an attempt to explain the adsorption mechanism and inhibition performance of two triazole derivatives, ie., 4-(benzylideneamino)-3-propyl-5-mercapto-1,2,4-triazole(BIPMT) and 4-(salicylidene amino)-3-propyl-5-mercapto-1,2,4-triazole (SIPMT), on mild steel using density functional theory (DFT) at the B3LYP/6-31G(d,p) level. Quantum chemical parameters such as E_{HOMO} (highest occupied molecular orbital energy), E_{LUMO} (lowest unoccupied molecular orbital energy), 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 ($\Delta E_{Back-donation}$) have been calculated. The local reactivity has been studied 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 obtained correlations and theoretical conclusions agree well with the experimental data.

Keywords: Triazole, corrosion inhibitors, reactivity, DFT, Fukui function, softness indices, electrophilicity index.

1. INTRODUCTION

The study of corrosion processes and their inhibition by organic compounds is a very active field of research. Over the years, considerable efforts have been deployed to find suitable corrosion inhibitors of organic origin in various corrosive media [1–3]. It has been commonly recognized that organic inhibitor usually promotes formation of a chelate on the metal surface, which includes the transfer of electrons from the organic compounds to metal, forming coordinate covalent bond during such chemical adsorption process [4]. In this way, the metal acts as an electrophile, whereas the nucleophile centers of inhibitor molecule are normally hetero atoms with free electron pairs which are readily available for sharing, to form a bond. Among efficient corrosion inhibitors used to prevent the deterioration of mild steel are heterocyclic organic compounds consisting of nitrogen, sulphur and/or oxygen atoms [5-7]. The planarity and the lone electron pairs in the hetero atoms are important features that determine the adsorption of molecules on the metallic surface [8]. The inhibition efficiency has been closely related to the inhibitor adsorption abilities and the molecular properties for different kinds of organic compounds [9-11]. The power of the inhibition depends on the molecular structure of the inhibitor. Organic compounds, which can donate electrons to unoccupied d orbital of metal surface to form coordinate covalent bonds and can also accept free electrons from the metal surface by using their anti bonding orbital to form feedback bonds, constitute excellent corrosion inhibitors.

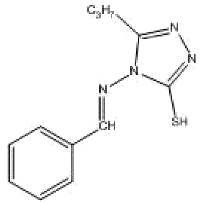
Free electron pairs on hetero atoms or π electrons are readily available for sharing to form a bond and act as nucleophile centres of inhibitor molecules and greatly facilitate the adsorption process over the metal surface, whose atoms act as electrophiles [12]. Recently the effectiveness of an inhibitor molecule has been related to its spatial as well as electronic structure [13, 14]. Quantum chemical methods have already proven to be very useful in determining the molecular structure as well as elucidating the electronic structure and reactivity [15]. Density functional theory (DFT) [16, 17] has provided a very useful framework for developing new criteria for rationalizing, predicting, and eventually understanding many aspects of chemical processes [18-22]. A variety of chemical concepts which are now widely used as descriptors of chemical reactivity, e.g., electronegativity [19] hardness or softness quantities etc., appear naturally within DFT. The Fukui function [21] represents the relative local softness of the electron gas, measures the local electron density/population displacements corresponding to the inflow of a single electron.

The reactive ability of the inhibitor is closely linked to their frontier molecular orbital (FMO), including highest occupied molecular orbital, HOMO, and lowest unoccupied molecular orbital, LUMO, and the other parameters such as hardness and softness. 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 [23, 24]. Although experimental work of M.A.Quraishi *et al.* [25] provide valuable information on the corrosion inhibition efficiency of 4-(benzylideneamino)-3-propyl-5-mercapto-1,2,4-triazole(BIPMT) and 4-(salicylideneamino)- 3-propyl-5-mercapto-1,2,4-triazole(SIPMT), a deep understanding of the inhibition property remain unclear. To date, however, no study has been performed to investigate the corrosion inhibition efficiency of SIPMT>BIPMT by using quantum chemical calculations. The objective of the present paper is to extend the study of M.A.Quraishi *et al.* [25] by analyzing the inhibitive properties of SIPMT and BIPMT using DFT calculations. These properties are: the molecular structure, the dipole moment, E_{HOMO}, E_{LUMO}, energy gap (ΔE), and those parameters that give valuable information about the reactive behavior: electronegativity (χ), global hardness (η) and the fraction of electrons transferred from the inhibitor molecule to the metallic atom (ΔN) and the back-donation($\Delta E_{\text{Back-donation}}$). 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. Results obtained showed that the inhibition efficiency of SIPMT>BIPMT. 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.

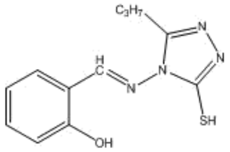
2. COMPUTATIONAL DETAILS

2.1. Quantum-chemical calculations methodology

In computational chemistry tools, the DFT offers the fundamentals for interpreting multiple chemical concepts used in different branches of Chemistry. In order to explore the theoretical-experimental consistency, quantum chemical calculations were performed with complete geometry optimizations using standard Gaussian-03 software package [26]. Geometry optimization were carried out by B3LYP functional at the 6-31G (d,p) basis set and at the density functional theory (DFT) level. 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 [27, 28]. 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 BIPMT and SIPMT are presented in Figure 2.

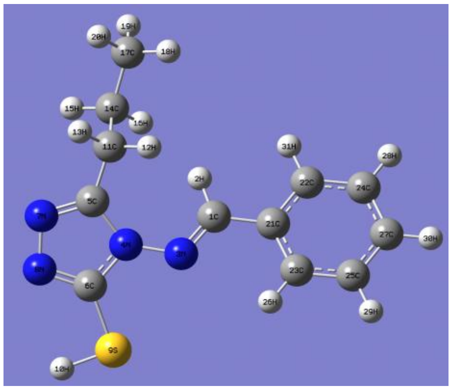


4-(benzylideneamino)-3-propyl-5-mercapto-1,2,4-triazole(BIPMT)

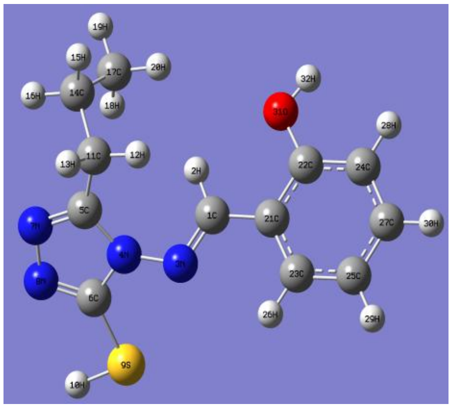


4-(salicylideneamino)-3-propyl-5-mercapto-1,2,4-triazole(SIPMT)

Fig. 1: Names, molecular structure and the abbreviation of the inhibitors investigated



BIPMT



SIPMT

Figure 2. Optimized molecular structure of BIPMT and SIPMT by B3LYP/6-31G (d,p)

3. RESULTS AND DISCUSSION

Density functional theory (DFT) [16] 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). According to Koopman's theorem [29] the ionization potential (IE) and electron affinity (EA) of the inhibitors are calculated using the following equations and hence χ and η are calculated.

$$IE = -E_{HOMO}$$
$$EA = -E_{LUMO}$$

The higher HOMO energy corresponds to the more reactive molecule in the reactions with electrophiles, while lower LUMO energy is essential for molecular reactions with nucleophiles [30].

$$\chi = \frac{IE + EA}{2}$$
$$\eta = \frac{IE - EA}{2}$$

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

$$S = \frac{1}{\eta}$$

Electronegativity, hardness and softness have proved to be very useful quantities in the chemical reactivity theory. The electronegativity of the inhibitor molecules is lower than the bulk iron. 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

$$\omega = \mu^2/2\eta$$

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 [31] 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 toward that of higher value, until the chemical potentials are the same. For the calculation the following formula was used [34].

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

Where χ_{Fe} and χ_{inh} denote the absolute electronegativity of iron and inhibitor molecule respectively η_{Fe} and η_{inh} denote the absolute hardness of iron and the inhibitor molecule respectively. In order to calculate the fraction of electrons transferred, the theoretical value for the electronegativity of bulk iron was used χ_{Fe}=7.0 eV [34] and a global hardness of η_{Fe} = 0 by assuming that for a metallic bulk I= A [35]. The difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as a resistance [31].

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 ΔE *Back-donation* implies that when $\eta > 0$ and ΔE *Back-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.

3.1. Theoretical assessment

The inhibition effect of inhibitor compound is usually ascribed to adsorption of the molecule on metal surface. There can be physical adsorption (physisorption) and chemical adsorption (chemisorption) depending on the adsorption strength. When chemisorption takes place, one of the reacting species acts as an electron pair donor and the other one acts as an electron pair acceptor. The energy of the highest occupied molecular orbital (E_{HOMO}) measures the tendency towards the donation of electron by a molecule [39]. High values of E_{HOMO} have a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy, empty molecular orbital. Increasing values of E_{HOMO} facilitate adsorption and therefore enhance the inhibition efficiency, by influencing the transport process through the adsorbed layer. Therefore, higher values of E_{HOMO} indicate better tendency towards the donation of electron, enhancing the adsorption of the inhibitor on mild steel and therefore better inhibition efficiency. 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 BIPMT and SIPMT is represented in figure 3. Table 1 represents the total energy and calculated energy levels in (eV) of the HOMO, LUMO and energy gap of the investigated molecules.

Table 1. Global chemical reactivity indices for BIPMT and SIPMT calculated using B3LYP/6-31G (d,p).

Parameters	BIPMT	SIPMT
E (au)	-1082.86706	- 1158.08684
E_{HOMO}(eV)	-6.089229	-5.916977
E_{LUMO} (eV)	-2.034913	-1.998449
Energy gap(ΔE) (eV)	4.054316	3.918528

According to the frontier molecular orbital theory (FMO) of chemical reactivity, transition of electron is due to interaction between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of reacting species [40]. 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 empty molecular orbital energy [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 feed back bond. According to our result, the highest E_{HOMO} value -5.916977 (eV) of SIPMT indicates the better inhibition efficiency.

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 %IE of the molecule. 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 [42]. Reportedly, excellent corrosion inhibitors are usually organic compounds which not only offer electrons to unoccupied orbital of the metal but also accept free electrons from the metal [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 table 1 shows that inhibitor SIPMT has the lowest energy gap, this means that the molecule could have better performance as corrosion inhibitor.

Table 2. Quantum chemical descriptors for inhibitor BIPMT and SIPMT calculated using B3LYP/6-31G (d,p).

Parameters	BIPMT	SIPMT
Ionization potential (IE) /(eV)	6.089229	5.916977
Electron affinity (EA) /(eV)	2.034913	1.998449
Chemical Potential (μ) /eV	-4.062071	-3.957713
Global Hardness(η) / eV	2.027158	1.959264
Electronegativity(χ) (eV)	4.062071	3.957713
Global softness(S)	0.493301	0.510396
Electrophilicity (ω)	4.069841	3.997289

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 [45]. The low ionization energy 5.916977 (eV) of SIPMT 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[46]. In our present study SIPMT with low hardness value 1.959264 (eV) compared with BIPMT, have a low energy gap. 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 [12]. 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 [47]. SIPMT with the softness value of 0.510396 has the highest inhibition efficiency.

According to Sanderson's electronegativity equalization principle [48], BIPMT 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 BIPMT>SIPMT. Hence an increase in the difference of electronegativity between the metal and the inhibitor is observed in the order SIPMT>BIPMT. 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 [49]. In our present study, SIPMT is the strongest nucleophile while BIPMT is the strongest electrophile.

The number of electrons transferred (ΔN) was also calculated and tabulated in Table 3. Values of ΔN show that the inhibition efficiency resulting from electron donation agrees with Lukovits's study [33]. If $\Delta N < 3.6$, 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: SIPMT>BIPMT. 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 (SIPMT), while the least fraction is associated with the inhibitor that has the least inhibition efficiency (BIPMT).

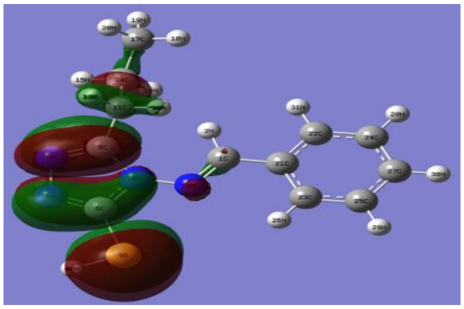
In Table 3, the calculated ΔE *back-donation* values for both, inhibitors are listed. The order followed is: SIPMT > BIPMT, which indicates that back-donation is favoured for the SIPMT, which is the best inhibitor.

Table 3. The number of electron transferred (ΔN) and ΔE back donation (eV) calculated for inhibitor BIPMT and SIPMT.

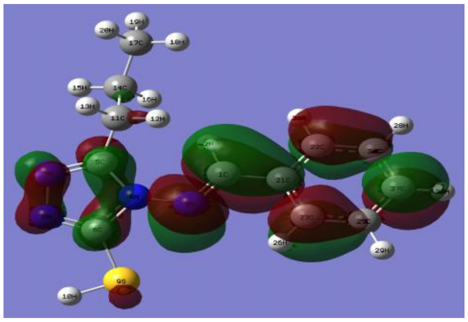
Parameters	BIPMT	SIPMT
Transferred electrons fraction (ΔN)	0.724514	0.776385
ΔE back-donation / (eV)	-0.5068795	-0.489816

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 [50]. There is a general consensus by several authors that the more negatively charged an heteroatom, is the more it can be adsorbed on the metal surface through the donor-acceptor type reaction [43]. 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.

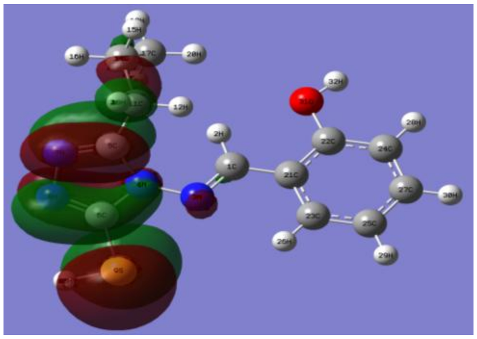
The local reactivity of molecule BIPMT and SIPMT is analyzed by means of the condensed Fukui function. The condensed Fukui function and local softness indices allow one distinguish each part of the molecule on the basis of its distinct chemical behaviour [51] due to the different substituted functional 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 nucleophilic attack the most reactive site of BIPMT and SIPMT is on the C (1). It is clear that C (1) atom of BIPMT and SIPMT has more nucleophilic character and is involved in the chemical reactivity of the molecules with metal surface which exhibit the adsorption mechanism. The Fukui function f_k^- is confirmed by the electrophilic attack at the site S(9) atom in both the compounds.



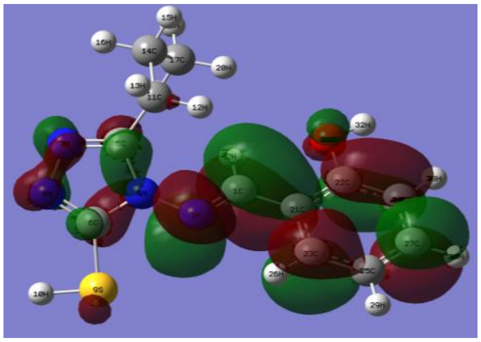
HOMO of BIPMT



LUMO of BIPMT



HOMO of SIPMT



LUMO of SIPMT

Figure 3. Frontier molecular orbital diagrams of BIPMT and SIPMT by B3LYP/6-31G (d,p)

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

Atom No	f_k^+	f_k^-	s_k^+	s_k^-
1 C	**0.118727**	0.009049	**0.058557**	0.004463
2 H	0.062009	0.028921	0.030583	0.014264
3 N	0.117778	-0.01167	0.058089	-0.005756
4 N	-0.04978	0.015923	-0.024552	0.007853
5 C	0.02179	0.056635	0.010747	0.027933
6 C	0.035723	-0.001869	0.017619	-0.000922
7 N	0.052461	0.115437	0.025874	0.056935
8 N	0.039193	0.1183	0.019330	0.058347
9 S	0.055277	**0.274722**	0.027263	**0.135497**
10 H	0.037219	0.0569	0.018356	0.028064
11 C	-0.004511	-0.025692	-0.002225	-0.012672
12 H	-0.021041	0.036609	-0.010378	0.018056
13 H	0.051108	0.050266	0.025207	0.024792
14 C	-0.016202	-0.014967	-0.007991	-0.007382
15 H	0.065624	0.017963	0.032366	0.008859
16 H	-0.005948	0.061947	-0.002933	0.030553
17 C	-0.005946	-0.013655	-0.002932	-0.006735
18 H	-0.022072	0.006764	-0.010886	0.003336
19 H	0.039413	0.044528	0.019439	0.021962
20 H	0.001421	-0.00276	0.000701	-0.001361
21 C	-0.022479	-0.009929	-0.011087	-0.004897
22 C	0.018233	0.014955	0.008993	0.007376
23 C	0.043185	0.010337	0.021299	0.005098
24 C	0.004773	0.003275	0.002354	0.001615
25 C	-0.001908	0.005097	-0.000941	0.002514
26 H	0.058831	0.007162	0.029016	0.003532
27 C	0.047661	0.015028	0.023507	0.007412
28 H	0.070945	0.03541	0.034991	0.017465
29 H	0.071419	0.032424	0.035225	0.015992
30 H	0.078861	0.039192	0.038895	0.01933
31 H	0.05824	0.023696	0.028725	0.011687

4. CONCLUSION

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 using density functional theory at B3LYP/6-31-G(d,p) basis set. The inhibition efficiency of the molecules BIPMT and SIPMT obtained quantum chemically increase with the increase in E_{HOMO}, and decrease in energy gap (ΔE). SIPMT 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. Comparison of theoretical and experimental data exhibit good correlation confirming the reliability of the method employed here.

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

Atom No	f_k^+	f_k^-	s_k^+	s_k^-
1 C	**0.161197**	0.012297	**0.082274**	0.006276
2 H	0.065617	0.017827	0.033491	0.009098
3 N	0.105634	-0.016117	0.053915	-0.008226
4 N	-0.046667	0.026711	-0.023818	0.013633
5 C	0.034453	0.048395	0.017585	0.024701
6 C	0.010977	0.005207	0.005603	0.002658
7 N	0.03512	0.118078	0.017926	0.060266
8 N	0.043947	0.108734	0.022430	0.055497
9 S	0.057385	**0.272314**	0.029289	**0.138988**
10 H	0.04293	0.053841	0.021911	0.027480
11 C	-0.011948	-0.02258	-0.006098	-0.011525
12 H	-0.023978	0.039101	-0.012238	0.019957
13 H	0.036143	0.051589	0.018447	0.026331
14 C	-0.004167	-0.021977	-0.002126	-0.011217
15 H	0.030368	0.049682	0.015499	0.025357
16 H	0.039434	0.021451	0.020127	0.010948
17 C	-0.01647	-0.007768	-0.008406	-0.003965
18 H	-0.029911	-0.010077	-0.015266	-0.005143
19 H	0.045429	0.042286	0.023187	0.021583
20 H	0.007927	0.015026	0.004046	0.007669
21 C	-0.0574	-0.010044	-0.029297	-0.005126
22 C	0.037102	0.02445	0.018937	0.012479
23 C	0.065133	0.01065	0.033244	0.005436
24 C	0.017506	0.007982	0.008935	0.004074
25 C	-0.004658	0.006346	-0.002377	0.003239
26 H	0.044703	0.006912	0.022816	0.003528
27 C	0.049891	0.012593	0.025464	0.006427
28 H	0.072417	0.035696	0.036961	0.018219
29 H	0.061614	0.033394	0.031447	0.017044
30 H	0.077454	0.039345	0.039532	0.020081
31 O	0.017882	0.009004	0.009127	0.002101
32 H	0.034935	0.019651	0.017831	0.004586

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