A Density Functional Theory (DFT) Computational Studies on Thiophene Oligomers as Corrosion Inhibitors of Aluminum

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Abstract

Theoretical Quantum chemical studies was performed on Thiophene oligomers as corrosion inhibitors of Aluminum, using density functional theory(DFT) at the B3LYP/6-31 G level (d) to search the correlation between the molecular structure and corrosion inhibitor efficiency. The calculated energy of highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and energy gap (ΔE = EHOMO- ELUMO). quantum chemical parameters such as , the total amount of electronic charge transferred,(ΔN) from the inhibitor to metallic surface, electrophilicity index (ω) (electrons transfer from metals to the anti π- orbital's of the inhibitors), chemical softness (σ) and chemical hardness (η) of Thiophene oligomers were reported. The interactions of these frontier molecular orbital's (ELUMOinh- EHOMOAl and ELUMOAl- EHOMOinh) with Aluminum reveal that charge transfer mechanism may be responsible for the binding or adsorption of these compounds onto the metal surface. It was found that the corrosion inhibitor efficiencies of oli Thiophene gomers increase with an increasing the number of Thiophene units in Thiophene oligomers structure, which is in agreement with the previous published experimental results .

Keywords: Aluminum, Corrosion, DFT, Inhibitor, Thiophene.

1. Corrosion inhibitor

Aluminium and its alloys constitute the most important material, after steel, for various different practical applications. The presence of an adherent and thin oxide layer onto aluminium, imparts high corrosion resistance in moderately corrosive media. However, in aggressive environments, the thin oxide film does not provide long-term corrosion resistance, resulting in localized attack of the substrate surface [1]. Therefore, different coating treatments of the aluminium surface are required to obtain major protection levels.

A corrosion inhibitor is a chemical compound that, when added to a liquid or gas, decreases the corrosion rate of a material, typically a metal or an alloy. The effectiveness of a corrosion inhibitor depends on fluid composition, quantity of water, and flow regime. A common mechanism for inhibiting corrosion involves formation of a coating, often a passivation layer, which prevents access of the corrosive substance to the metal. Permanent treatments such as chrome plating are not generally

considered inhibitors, however. Instead corrosion inhibitors are additives to the fluids that surround the metal or related object.

1.1Molecular orbital energies

Highest occupied molecular orbital energy (E_{HOMO}) and lowest unoccupied molecular orbital energy (E_{LUMO}) are very popular quantum chemical parameters. These orbital's, also called the frontier orbital's, determine the way the molecule interacts with other species. The HOMO is the orbital that could act as an electron donor, since it is the outermost (highest energy) orbital containing electrons. The LUMO is the orbital that could act as the electron acceptor, since it is the lowest energy orbital that has room to accept electrons. According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between the frontier orbital's (HOMO and LUMO) of reactants [2]. The energy of the HOMO is directly related to the ionization potential and the energy of the LUMO is directly related to the electron affinity with the reverse in sign. The LUMO–HOMO gap, i.e. the difference in energy between the HOMO and LUMO, is an important stability index [3]. A large LUMO–HOMO gap implies high stability for the molecule in chemical reactions [4]. The concept of ‘‘activation hardness” has been also defined on the basis of the LUMO–HOMO energy gap. The qualitative definition of hardness is closely related to the polarizability, since a decrease of the energy gap usually leads to easier polarization of the molecule [5].

The aim of this study

The aim of this work is to perform a theoretical calculation on aluminum using DFT calculation by calculating E_{HOMO}, E_{LUMO}, ΔE (E_{LUMO}-E_{HOMO}), softness, hardness, electron transfer from inhibitor to metal and electrophilicity, and comparing these items with the experimental results.

2- Results and discussion.

The thiophene Oligomers under investigation and there structures are shown in Scheme.1, the energy of the frontier molecular orbital's, (E_{HOMO} and E_{LUMO}), the energy gap (ΔE),the chemical softness (σ),the chemical hardness (η), and the fraction of the electron transferred (ΔN), and elecrophilicity index (ω), were calculated according to molecular orbital theory [6]. The E_{HOMO}) and E_{LUMO} of the inhibitor are related to ionization potential(I) and electron affinity (*A*) respectively , with reversed sign .

$I = - E_{HOMO}$ …….(1)

$A = - E_{LUMO}$ ……..(2)

The higher the HOMO energy the more reactive molecule in the reactions with electrophiles, whereas lower LUMO energy is essential for molecular reactions with nucleophiles [7]. Electronegativity χ and chemical hardness η of the inhibitor are calculated according to the following formula:

$\chi = \left(\frac{I+A}{2}\right)$ ……..(3)

$\eta = \left(\frac{I-A}{2}\right)$……(4)

the global softness (σ) is the inverse of the chemical hardness [16]

$\sigma = \frac{1}{\mu}$.....(5)

Electronegativity, hardness and softness have proved to be very useful quantities in the chemical reactivity theory. When two systems, metal and inhibitor, are brought in contact together, electrons will flow from lower (χ) inhibitor to higher (χ) metal, until the chemical potentials become equal. The fraction of transferred electronic charge (ΔN) from the inhibitor molecule to the metallic atom was calculated according to Pearson [8]. For a reaction of two systems with different electronegativities (as a metallic surface and an inhibitor molecule) the following mechanism will take place: The difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as a resistance [9]. The global electrophilicity index was introduced by Parr et al. and is given by:

$\omega = \frac{\mu^2}{2\eta}$ .....(6)

electronic flow will occur from the molecule with the lower electronegativity value toward that of higher value, until the chemical potentials are the same.

For ΔN calculation, the following formula was used. [10]

$$\Delta N = \frac{\chi_{metal} - \chi_{inh}}{2(\eta_{metal} + \eta_{inh})} \quad .....(7)$$

Where χ_{metal} and χ_{inh} denote the absolute electronegativity of metal and inhibitor molecule respectively, η_{metal} and η_{inh} denote the absolute hardness of metal and the inhibitor molecule respectively.

Where μ represent the chemical potential and equal to the negative of electronegativity χ.[11]. According to the definition, this index measures the propensity of chemical species to accept electrons.

Table1 Calculated HOMO-LUMO energies of the inhibitors thiophene oligomers by DFT method.

Compounds	E_{HOMO}(eV)	E_{LUMO}(eV)
Al	-5.9857*	-0.4328*
Thiophene 1	-6.4867	-0.4065
Thiophene 2	-5.6146	-1.4800
Thiophene 3	-5.2739	-1.9402
Thiophene 4	-5.0978	-2.1935
Thiophene 5	-4.9933	-2.3522
Thiophene 6	-4.9259	-2.4594
Thiophene 7	-4.8801	-2.5356
Thiophene 8	-4.8478	-2.5925
Thiophene 9	-4.8241	-2.6357
Thiophene 10	-4.8061	-2.6695

*From ref [15].

The energy of the highest occupied molecular orbital (E_{HOMO}) measures the tendency towards the donation of electron by a molecule [12]. High values of E_{HOMO} have a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy, empty molecular orbital. Therefore, higher values of E_{HOMO} indicate better tendency towards the donation of electron. 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. 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 [13]. 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 [14]. The energies of HOMO and LUMO values of aluminum (Al) were compared to the values calculated for thiophene oligomers to determine the appropriate type of the interaction.The interaction energy of the HOMO- LUMO gap of aluminum- inhibitors thiophene oligomers are given in Table 2.

Table 3. Calculated quantum chemical parameters for thiophene oligomers with Al using DFT method.

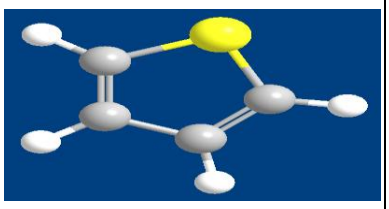
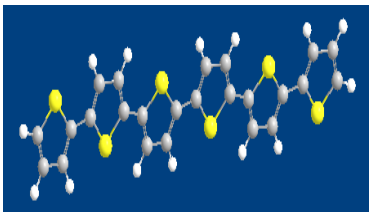
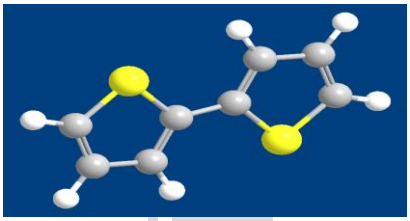
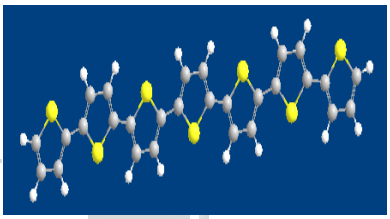
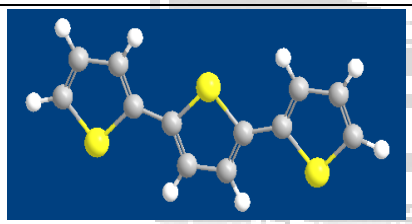
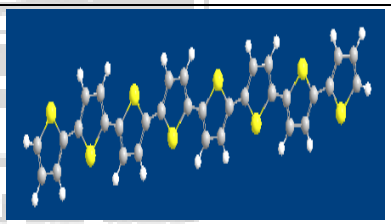
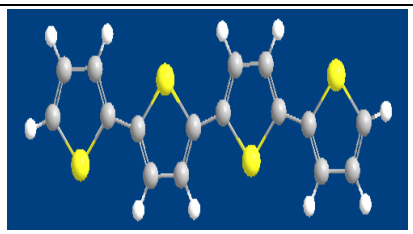
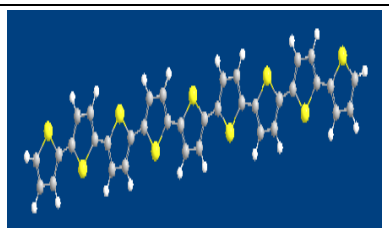
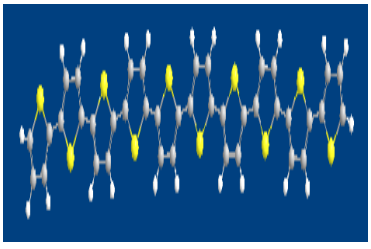
Quantum parameters	Thiophene1	Thiophene2	Thiophene3	Thiophene4	Thiophene5	Thiophene6	Thiophene7	Thiophene8	Thiophene9	Thiophene10
E_{HOMO}	-6.4867	-5.6146	-5.2739	-5.0978	-4.9933	-4.9259	-4.8801	-4.8478	-4.8241	-4.8061
E_{LUMO}	-0.4065	-1.4800	-1.9402	-2.1935	-2.3522	-2.4594	-2.5356	-2.5925	-2.6357	-2.6695
ΔEgap	6.0802	4.1346	3.3337	2.9043	2.6411	2.4665	2.3445	2.2553	2.1884	2.1366
I	6.4867	5.6146	5.2739	5.0978	4.9933	4.9259	4.8801	4.8478	4.8241	4.8061
A	0.4065	1.4800	1.9402	2.1935	2.3522	2.4594	2.5356	2.5925	2.6357	2.6695
X	3.4466	3.5473	3.6071	3.6457	3.6728	3.6927	3.7079	3.7202	3.7299	3.7378
η	3.0401	2.0673	1.6669	1.4522	1.3206	1.2333	1.1723	1.1277	1.0942	1.0683
σ	0.3289	0.4837	0.5999	0.6886	0.7572	0.8108	0.8530	0.8868	0.9139	0.9361
ΔN	0.0204	0.0349	0.0448	0.0516	0.0566	0.0603	0.0631	0.0654	0.0673	0.0687
ω	1.9537	3.0434	3.9028	4.5762	5.1073	5.5283	5.86439	6.1363	6.3572	6.5389

χ_{Al} = 3.2093 eV η_{Al} = 2.7764 eV

The energy gap (Table 3), ($\Delta E = E_{LUMO} - E_{HOMO}$) 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, lower values of the energy difference will render good inhibition efficiency [16]. Ionization energy is a fundamental descriptor of the chemical reactivity of atoms and molecules. High ionization energy indicates high stability and chemical inertness and low ionization energy indicates high reactivity of the atoms and molecules [17]. The low ionization energy 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 [18].

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 [19]. The global electrophilicity index measures the propensity of chemical species to accept electrons. 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 [20].From these calculations it can be seen that the energy gap (ΔE), ionization energy (I) and hardnees (η) decrease with increasing in the number of thiophene molecules while the electron affinity (A), electronegativity (χ), softnees (σ), electrophilicity (ω) and (ΔN) increase with increasing in the number of thiophene molecules.

Scheme1.The optimized molecular structures of thiophene oligomers under investigation are given in Figures (1-10).

Inhibitor	Structure	Inhibitor	Structure
Thiophene 2		Thiophene 6	
Thiophene 2		Thiophene 7	
Thiophene 3		Thiophene 8	
Thiophene 4		Thiophene 9	
Thiophene 5		Thiophene 10	

CONCLUSIONS

It can be concluded that thiophene oligomers can be a good inhibitors for aluminum The adsorption of the inhibitor on the metal surface is spontaneous. This study, thus displays a good correlation between theoretical and experimental data which confirm the reliability of the DFT method to study the inhibition corrosion of metal surface.

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