Theoretical Calculations of Pyrrole oligomers as Corrosion Inhibitors of Iron

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ABSTRACT

We have performed a DFT calculations on pyrrole oligomers as corrosion inhibitors of iron with complete optimization of geometries using BLYP/66-31G level (d) to find a relation between the molecular structure and corrosion inhibition.

The Highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Molecular Orbital (LUMO), and energy gap (ΔE = ELUMO - EHOMO) of pyrrole oligomers (1 to10) were calculated. The interactions of these frontier molecular orbitals (HOMO and LUMO) of the pyrrole oligomers as inhibitors with both iron (ELUMOinh - EHOMOFe) and (ELUMO Fe- EHOMOinh), were reported. Quantum chemical parameters such as electro negativity (χ), hardness (η), softness (σ), the fractions of electrons transferred (ΔN), electrophilicity index (ω), used to explain the electron transfer mechanism between the inhibitor molecules and the metal surface.

Keys word: - Iron, DFT, Corrosion, Inhibitor, pyrrole.

1. INTRODUCTION

Corrosion concern for industry, may cause reduced service life or complete failure of manufactured parts and finished goods. These issues directly impact the cost efficiency of the manufacturing process and cost of the finished goods, Corrosion inhibitors can be used to prevent the problems associated with corrosion. Corrosion is the destructive attack to metal by a chemical or electrochemical reaction with its environment. The terms corrosion and rusting are often used interchangeably the term "rust" typically is applicable to ferrous materials, iron and steel.

the most term to use is "corrosion " because it is inclusive of non-ferrous metals as well metallic staining.

corrosion is the destructive attack of metal or alloy chemically or electrochemically against its environment which leads to loss of useful properties of materials [1].

The protection of metals against corrosion can be achieved by adding inhibitors in small concentrations to its environment [2].

a survey of literature presents the applicability of organic compounds, particularly those containing O, S and N atoms in their long carbon chain/ aromatic structure, as corrosion inhibitors for mild steel in acidic media [3].

Corrosion at amount of metal is wasted by corrosion. It can cause tremendous economic damages. Minimizing this corrosion can save substantial money and prevent accidents due to equipment failure. Corrosion has and continues to be the research object of scientists [4, 5]. metal surfaces are a severe industrial problem. a large

Aim of the present work theoretical calculations have been performed on pyrrole oligomers as corrosion inhibitors of iron using DFT calculations by calculating {Highest occupied molecular orbital (HOMO)}, {lowest unoccupied molecular orbital (LUMO)}, energy gap, dipole moments, and comparing these items with the experimental results.

Corrosion protection by conducting polymers is a really new approach. In the last years, many researchers have studied the anti-corrosion activity of conducting polymers. Polypyrene (ppy) have been investigated intensively. The following part presents in more detail an overview of corrosion of corrosion protection using ppy. therefore, more theoretical insight is needed to study the interaction of inhibitor with metal surface using quantum chemical methods.

2- Results and Discussion

The optimized molecular structures of these pyrrole oligomers (1 to 10) are given in Figures 1. quantum chemical parameters such as the highest occupied molecular orbital energy(E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), electro negativity (χ), hardness (η), softness (σ), the fractions of electrons transferred (ΔN), electrophilicity index (ω), used to explain the electron transfer mechanism between the inhibitor molecules and the metal surface.

$\Delta E(gap) = E_{LUMO} - E_{HOMO}$

The ionization potential (I) and electron affinity (A) are related in turn to E_{HOMO} and E_{LUMO} [6]:

$$I = - E_{HOMO} \quad \text{and} \quad A = - E_{LUMO}$$

These quantities are related to electron affinity (A) and ionization potential (I) using the equation:

$$(\chi = \frac{I+A}{2}) \, , \, (\eta = \frac{I-A}{2})$$

A new global chemical reactivity parameter has been introduced and is called an electrophilicity index (ω), it is defined as [7].

$$(\omega = \frac{\mu^2}{2\eta}) \, , \, (\mu = - \chi)$$

Where μ represents the chemical potential. This was proposed as a measure of the electrophonic power of a molecule, global softness can also be defined as [8]:

$$(\sigma = \frac{1}{\eta}) \qquad (8)$$

The number of transferred electrons (ΔN) from the inhibitor molecule to the metal surface can be calculated by using the following equation [9]:

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

Where χ_{metal} and χ_{inh} denote the absolute electro negativity of iron and the inhibitor molecule, respectively, η_{metal} and η_{inh} denote the absolute hardness of metal and the inhibitor molecule, respectively, the difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as resistance [10].

The calculated results of the energies of frontier molecular orbitals for the inhibitors are given in Table 1.

Table1: The calculated HOMO-LUMO energies of inhibitor Pyrrole oligomers by DFT Method.

Compounds	E_{HOMO} (eV)	E_{LUMO} (eV)
Fe	-7.9024*	- 0.1510*
Py1	-5.5748	1.2645
Py2	-4.8142	0.2438
Py4	-4.3016	-0.3902
Py5	-4.2006	-0.5197
Py6	-4.1448	-0.5972
Py7	-4.0950	-0.6675
Py8	-4.0700	-0.7061
Py9	-4.0474	-0.7434
Py10	-4.0294	-0.7698
Py10	-4.0294	-0.7698

*****From ref. [11].

According to the frontier molecular orbital (FMO) theory, the chemical reactivity is a function of the in traction between the HOMO and LUMO levels of the reacting species [12,13] E_{HOMO} is a quantum chemical parameter which is associated with the electron donating ability of the molecule. A high value of ELUMO is likely to indicate a tendency of the molecule of low empty molecular orbital energy [14].

The energy of the lowest unoccupied molecular orbital, E_{LUMO}, indicates the ability of the molecule to accept electrons [15].

So, the lower the value of ELUMO, the more the molecule accepts electrons.

Thus, the binding ability of the inhibitor to the metal surface increases with increasing HOMO and decreasing LUMO energy values. The energies of HOMO and LUMO [16] for iron were compared to the values calculated for the pyrrole oligomers to determine the type of

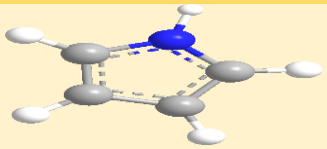
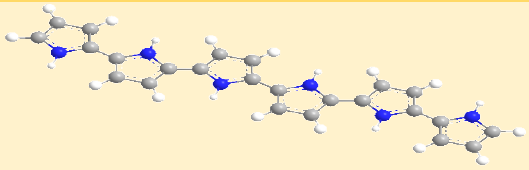
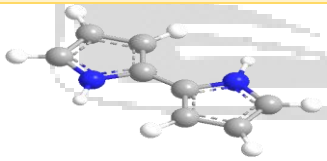
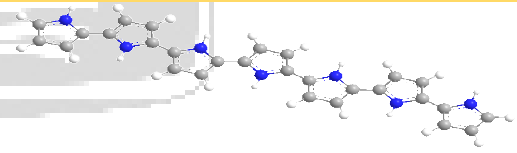
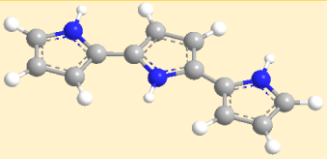
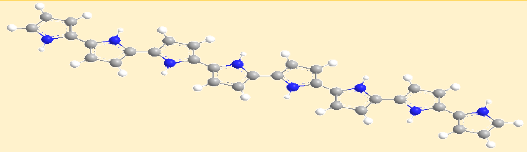
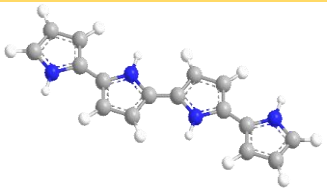
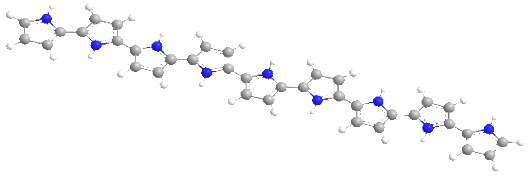
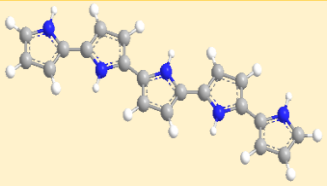
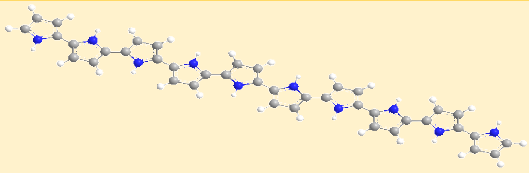
Inhibitor	Structure	Inhibitor	Structure
Pyrrole1		**Pyrrole6**	
Pyrrole2		**Pyrrole7**	
Pyrrole3		**Pyrrole8**	
Pyrrole4		**Pyrrole9**	
Pyrrole5		**Pyrrole10**	

Figure 1. Optimized molecular structures of pyrrole oligomers

interaction mated−inhibitors are given in Table 2. and all computes quantum chemical parameters are given in Table 3.

Table 2: HOMO-LUMO gap interactions of Iron –inhibitor by DFT Method.

Inhibitors	$(LUMO)_{inh}$ - $(HOMO)_{Fe}$	$(LUMO)_{Fe}$ – $(HOMO)_{inh}$
Py1	9.1669	5.4238
Py2	8.1462	4.6638
Py3	7.7358	4.3272
Py4	7.5121	4.1506
Py5	7.3826	4.4965
Py6	7.3051	3.9938
Py7	7.2349	3.9440
Py8	7.1962	3.9190
Py9	7.1591	3.8964
Py10	7.1325	3.8784

From Table 2, it can be seen that iron will act as a Lewis base while the inhibitors pyrrole oligomers act as a Lewis acid. So, iron will utilize the HOMO orbital to initiate the reaction with LUMO orbital of the pyrrole oligomers. The interaction will have certain amount of ionic character because the values of $LUMO_{inh}$ - $HOMO_{Fe}$ gap fall between 5 and 3 eV. Strong covalent bond can be expected only if $LUMO_{inh}$-$HOMO_{Fe}$ gap is approximately zero eV [15] It can be seen from Table 3. that iron will act as a Lewis acid while the inhibitors pyrrole oligomers act as a Lewis a base Table 3. In this case, pyrrole oligomers act as anodic inhibitor.

The Separation energy, $\Delta E_{gap} = (E_{LUMO} - E_{HOMO})$, is an important parameter Table 3.3 and it is a function of the reactivity of the inhibitor molecule towards the adsorption on metallic surface. As ΔE_{gap} decreases, the reactivity of the molecule increases leading to increase in the inhibitor efficiencies [16]. The effectiveness of pyrrole oligomers as inhibitors has been further addressed by evaluating the global reactivity parameters such as the electronegativity, χ ,the global chemical hardness, η, the global softness, σ, the fraction of electrons transferred, ΔN, from the inhibitor to iron, and the electrophilicity, ω, are tabulated in Table3.

Table3. Calculated quantum chemical parameters for pyrrole oligomers and iron by DFT method

Quantum parameter	Py1	Py2	Py3	Py4	Py5	Py6	Py7	Py8	Py9	Py10
E_{HOMO}	-5.5748	-4.8148	-4.4782	-4.3016	-4.2006	-4.1448	-4.0950	-4.0700	-4.0475	-4.0294
E_{LUMO}	1.2645	0.2438	-0.1665	-0.3902	-0.5197	-0.5972	-0.6675	-0.7061	-0.7434	-0.7698
ΔE(gap)	6.8393	5.0586	4.3116	3.9113	3.6809	3.5475	3.4275	3.3639	3.3040	3.2596
I(eV)	5.5748	4.8148	4.4782	4.3016	4.2006	4.1448	4.0950	4.0700	4.0475	4.0294
A(eV)	-1.2645	-0.2438	0.1665	0.3902	0.5197	0.5972	0.6675	0.7061	0.7434	0.7698
X(eV)	2.1551	2.2855	2.3223	2.3459	2.3601	2.3710	2.3812	2.3880	2.3954	2.3996
(eV)η	3.4196	2.5293	2.1558	1.9556	1.8404	1.7737	1.7137	1.6819	1.6520	1.6298
σ	0.2924	0.3953	0.4638	0.5113	0.5433	0.5637	0.5835	0.5945	0.6053	0.6135
ΔN	0.1282	0.1359	0.1412	0.1441	0.1457	0.1465	0.1471	0.1474	0.1475	0.1477
ω	0.6791	1.0293	1.2508	1.4069	1.5133	1.5847	1.6953	1.6953	1.7366	1.7665

X_{Fe}= 4.0267 , η_{Fe}= 3.8757

CONCLUSIONS

It was found that the interactions of the pyrrole oligomers with iron have certain ionic character by both DFT method, because the values of (ELUMOFe -EHOMOinh) gap fall between 5 and 3eV. Strong covalent bond can be expected only if gap is approximately zero eV.

We conclude that poyrrole oligomers be a good inhibitor for iron, this study thus displays a good correlation between theoretical and experimental data which confirms the reliability of the DFT method study the inhibition of corrosion of metal surfaces.

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