دراسات حسابية DFT و PM3 لبوليمرات البيرول كمثبطات (كموانع) لتآكل الألمونيوم

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DFT and PM3 calculation Studies on Pyrrole Oligomers as Corrosion Inhibitors of Aluminum

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الملخص العربي :

تم إجراء الدراسات الكيميائية النظرية الكمية على بوليمرات البيرول كمثبطات (كموانع) لتآكل الألمنيوم باستخدام نظرية **دالة الكثافة** (DFT) على مستوى B3LYP/6-31 G (d) والطريقة الشبه تجريبية (PM3) للبحث في العلاقة بين التركيب الجزيئي لكفاءة مثبطات التآكل و حساب أعلى طاقة فلك جزيئي مشغول (E_{HOMO}) وأقل طاقة فلك جزيئي غير مشغول (E_{LUMO})، وطاقة الفجوة ($\Delta E = E_{LUMO} - E_{HOMO}$) لبوليمرات البيرول (1 إلي 10). المعاملات الكيميائية الكمية مثل كمية الشحنة الإلكترونية المنقولة (ΔN) من المانع إلي السطح المعدني و الألكتروفليستي (ω) انتقال الإلكترونات من المعادن إلي أفلاك ضد الترابط π للمثبطات) و الليونة (σ) و الصلابة الكيميائية (η)) لبوليمرات البيرول، حساب التفاعل المتبادل بين هذه الأفلاك لهذه البوليمرات مع الألمنيوم $(HOMO)_{inh}$-$(LUMO)_{Al}$ and $(HOMO)_{Al}$-$(LUMO)_{inh}$. أن الية نقل الشحنة قد تكون مسؤولة عن ربط هذه المركبات أو امتزازها على سطح المعدن.وقد وجدت أن كفاءة

مثبطات التآكل لبوليمرات البيرول تزداد بزيادة عدد وحدات البوليمر في بنية لبوليمرات البيرول والتي تتفق مع النتائج التجريبية المنشورة السابقة.

Abstract

Theoretical Quantum chemical studies was performed on Pyrrole oligomers as corrosion inhibitors of Aluminum, using density functional theory(DFT) at the B3LYP/6-31 G level (d) and semi-empirical methods(PM3) 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 ($\Delta E = E_{HOMO} - E_{LUMO}$) for Pyrrole oligomers (1 to 10) were calculated. Quantum chemical parameters such as , the total amount of electronic charge transferred,(□N) from the inhibitor to metallic surface, electrophilicity index (□) (electrons transfer from metals to the anti π- orbitals of the inhibitors), chemical softness (σ) and chemical hardness (η) of Pyrrole oligomers were reported. The interactions of these frontier molecular orbital's ($E_{LUMOinh} - E_{HOMOAl}$ and $E_{LUMOAl} - E_{HOMOinh}$) 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 Pyrrole oligomers increase with an increasing the number of Pyrrole units in Pyrrole oligomers structure, which is in agreement with the previous published experiment

Keys word:- DFT,PM3, Corrosion, Inhibitor, pyrrole oligomers, Aluminum.

1.Introduction

Corrosion is the gradual destruction of material, usually metals, by chemical reaction with its environment. In the most common use of the word, this means electrochemical oxidation of metals in reaction with an oxidant such as oxygen. Rusting, the formation of iron oxides, is a well-known example of electrochemical corrosion. This type of damage typically produces oxide(s) or salt(s) of the original metal. Corrosion can also occur in materials other than metals, such as ceramics or polymers, although in this context, the term degradation is more common. Corrosion degrades the useful properties of materials and structures including strength, appearance and permeability to liquids and gas [1]. A corrosion inhibitor is a chemical compound that, when added to a liquid or gas, decreases the corrosion rates of a material, typically a metal or an alloy [2]. 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 surrounds the metal or related object [3].

1.1.Parametric Model 3 (PM3)

PM3 (Parametric Model 3) is a variation of AM1, differing mainly in how the parameterization is done [4]. In contrast, semi-empirical methods employ empirically determined parameters and are thus less attractive to the theoretical purist. However, semi-empirical methods are fast enough and accurate enough for routine application to quite large systems. In consequence, a few semi-empirical methods, in particular modified neglect of diatomic overlap (MNDO), have become very popular.

1.2. Density function theory (DFT)

This theory is based on electron density function ρ which is considerably simpler function than wave function Ψ. Thus the energy of the molecule can be determined from electron density instead of wave function and takes less computational time than other ab initio methods with similar accuracy. Density functional theory is similar in mathematical form to Hartree-Fock (HF) method. The electron density function is expressed as linear combination of basic functions. Then determinant is formed from this function using variation method for determining the energy of the molecule. The exact density functional is not known. Therefore, there is a list of different functional were developed from quantum mechanics and some were developed by parameterizing functions in order to produce experimental results. Therefore, one can consider DFT as ab initio or a class by itself [5]. This theory has been developed more recently than other ab initio methods. Because of this, there are classes of problems not yet explored with this theory, making it all the more crucial to test the accuracy of the method before applying it to unknown systems [6]. There are several versions of DFT and the most popular one is called B3LYP. It is due to Beck who argued that some of the deficiencies of the empirical exchange-correlation functional may be overcome by incorporating some HF exchange. Combined with the 6-31G(d) basis, B3LYP has become the method of choice for efficient and accurate computation of most chemical properties. It has been shown to provide a significant improvement over Hartree-Fock and semi-empirical and even MP2 methods for the study of organic reactions [7]. Also, B3LYP performs very well for molecular geometries, force fields, hydrogen-bonding energies, and bond dissociation energies. The accuracy of results tends to degrade significantly with the use of very small basis sets. For accuracy considerations, the smallest basis set used is generally 6-31 G* [8].

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} [9]:

$I= - E_{HOMO}$ and $A= - E_{LUMO}$

The ionization potential (I) and electron affinity (A) are related in turn to E_{HOMO} and E_{LUMO} [9]:

$I= - E_{HOMO}$ and $A= - E_{LUMO}$

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

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

A new global chemical reactivity parameter has been introduced and is called an electrophilicity index (ω), it is defined as [10].

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

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 [11]:

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

The number of transferred electrons (ΔN) from the inhibitor molecule to the metal surface can be calculated by using the following equation [12]:

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

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 matal and the inhibitor molecule, respectively, the difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as resistance [13]. The calculated results of the energies of frontier molecular orbital's for the inhibitors are given in Table 1.

2.1. PM3 calculations

Table 1. The calculated (HOMO-LUMO) energies of the inhibitors by PM3 method

Compounds	E_{HOMO} (eV)	E_{LOUM} (eV)
Al	-5.9857*	- 0.4328*
Py1	-9.4202	0.9166
Py2	-8.5412	0.0503
Py3	-8.2368	-0.2485
Py4	-8.0897	-0.4050
Py5	-8.0035	-0.4891
Py6	-7.9534	-0.5381
Py7	-7.9168	-0.5732
Py8	-7.8920	-0.5919
Py9	-7.8680	-0.6072
Py10	-7.8681	-0.6230

* Form ref. [14].According to the frontier molecular orbital (FMO) theory, the chemical reactivity is a function of the interaction between the HOMO and LUMO levels of the reacting species [15]. E_{HOMO} is associated

with the electron donating ability of the molecule.A high value of EHOMO indicates a tendency of the molecule to donate electrons to the appropriate acceptor molecule of low empty molecular orbital energy [18]. The energy of the lowest unoccupied molecular orbital, E_{LUMO}, indicates the ability of the molecule to accept electron [17]; 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 [18] for aluminum were compared to the values calculated for the aluminum compounds to determine the type of the interaction. LUMO-HOMO gaps for the interaction aluminum-inhibitors are given in Table 2, and all computed quantum chemical parameters are given in Table 3.

Table 2. HOMO-LUMO gap interaction of Al with the inhibitors byPM3 Method.

Inhibitors	$(LUMO)_{inh}$ - $(HOMO)_{Al}$	$(LUMO)_{Al}$ – $(HOMO)_{inh}$
Py1	6.9024	8.9874
Py2	6.0361	8.1084
Py3	5.7372	7.8040
Py4	5.5807	7.6565
Py5	5.4966	7.5707
Py6	5.4476	7.5206
Py7	5.4124	7.4840
Py8	5.3938	7.4598
Py9	5.3785	7.4351
Py10	5.3627	7.4350

Aluminum will act as Lewis base while the inhibitor pyrrole oligomers act as Lewis acids. It can be seen from Table2.

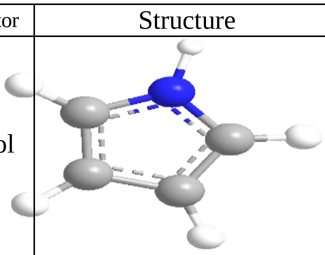
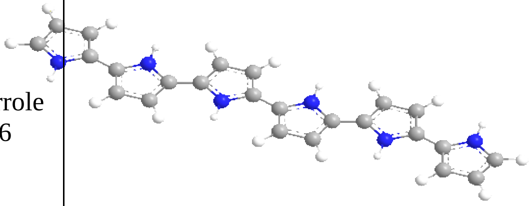
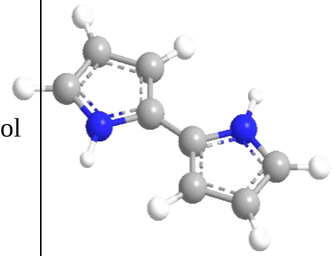
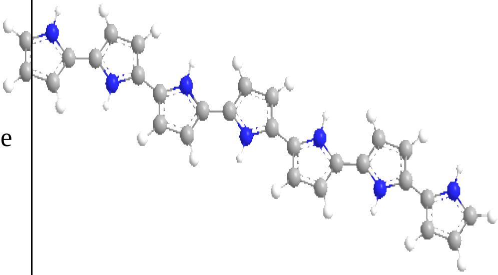
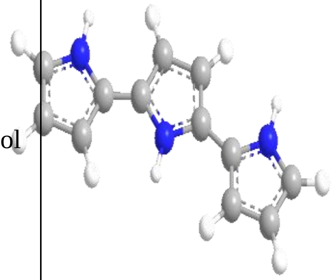
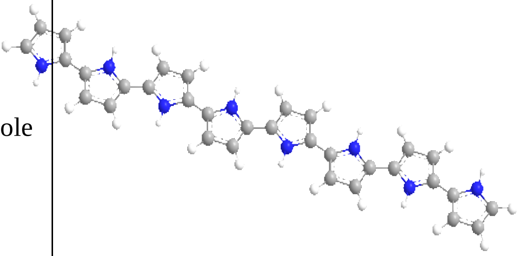
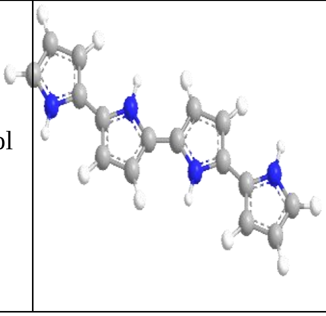
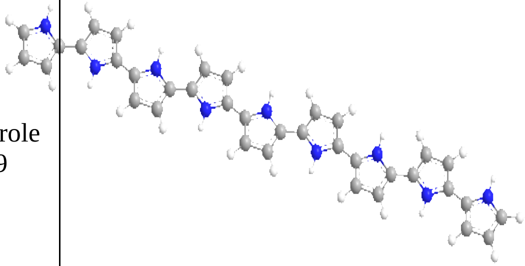
that pyrrole oligomers act as cathodic inhibitor. The interaction will have certain amount of ionic character because the energy values of $LUMO_{inh}$ -$HOMO_{Al}$ gap lie between 6 to 5 eV. The calculated quantum parameters are given in Table 3. It can be seen that an increase in ΔN values result from an increase in the number of pyrrole moleculesbut the values of ΔN are slightly higher. This may be due to stronger interaction electron aluminum and the inhibitor. Also the increase in the values of ω may be d ue to the same reason.

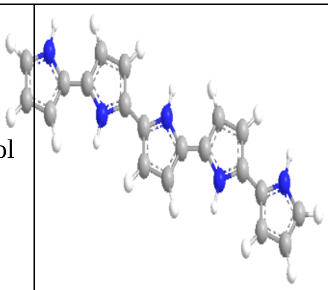
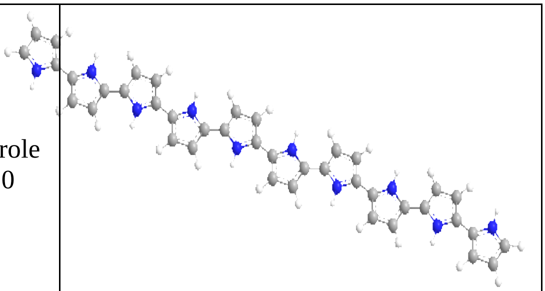
Table3. Calculated quantum Chemical parameters for pyrrole oligomers and aluminum using PM3 method.

Quantum parameter	E_{HOMO}	E_{LUMO}	ΔE(gap)	I(eV)	A(eV)	X(eV)	η(eV)	Σ	ΔN	Ω
Py1	-9.4202	0.9166	10.3369	9.4202	-0.9166	4.2517	5.1684	0.1934	0.0656	1.7488
Py2	-8.5412	0.0503	8.5916	8.5412	-0.0503	4.2454	4.2958	0.2327	0.0732	2.0978
Py3	-8.2368	-0.2485	7.9882	8.2368	0.2485	4.2426	3.9941	0.2503	0.0763	2.2533
Py4	-8.0897	-0.4050	7.6847	8.0897	0.4050	4.2473	3.8423	0.2602	0.0784	2.3475
Py5	-8.0035	-0.4891	7.5143	8.0035	0.4891	4.2463	3.7571	0.2661	0.0793	2.3995
Py6	-7.9534	-0.5381	7.4152	7.9534	0.5381	4.2458	3.7076	0.2697	0.0799	2.4310
Py7	-7.9168	-0.5732	7.3435	7.9168	0.5732	4.2450	3.6717	0.2723	0.0803	2.4539
Py8	-7.8920	-0.5919	7.3001	7.8920	0.5919	4.2420	3.6500	0.2739	0.0804	2.4612
Py9	-7.8680	-0.6072	7.2607	7.8680	0.6072	4.2376	3.6303	0.2754	0.0803	2.4732
Py10	-7.8681	-0.6230	7.2451	7.8681	0.6230	4.2455	3.6225	0.2760	0.0809	2.4878

X_{Al}= 3.2093 , η_{Al}= 2.7

Figure 1 .Optimized molecular structures of pyrrole oligomers.

Inhibitor	Structure	Inhibitor	Structure
Pyrrole1		Pyrrole 6	
Pyrrole2		Pyrrole 7	
Pyrrole3		Pyrrole 8	
Pyrrole4		Pyrrole 9	

Pyrrole5		Pyrrole 10	

2.2. DFT calculations

Table 4.. The calculated (HOMO-LUMO) energies of the inhibitors by DFT method.

Compounds	E_{HOMO} (eV)	E_{LUMO} (eV)
Al	-5.9857*	- 0.4328*
Py1	-5.5748	1.2645
Py2	-4.8142	0.2438
Py3	-4.4782	-0.1665
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

*From ref. [14].

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 [19,20] E_{HOMO} is a quantum chemical parameter which is associated with the electron donating ability of the molecule. A high value of E_{LUMO} is likely to indicate a tendency of the molecule of low empty molecular orbital energy [21]. The energy of the lowest unoccupied molecular orbital, E_{LUMO}, indicates the ability of the molecule to accept electrons [22]. So the lower the value of E_{LUMO}, 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 [23] for aluminum were compared to the values calculated for the pyrrole oligomers to determine the type of interactin matel–inhibitors are given in Table 5. and all computes quantum chemical parameters are given in Table 5. The interaction energies of the HOMO-LUMO gap of aluminum-inhibitor are given in Table 5. Aluminum will act Lewis acid and the inhibitors pyrrole oligomers act as a Lewis base. Pyrrole oligomers act as anodic inhibitor.

Table5. HOMO-LUMO gap interactions of aluminum-inhibitor pyrrole oligomers by DFT Method.

Inhibitor	$(LUMO)_{inh}$ - $(HOMO)_{Al}$	$(LUMO)_{Al}$– $(HOMO)_{inh}$
Py1	7.2502	5.1420
Py2	6.2295	4.3820
Py3	5.8192	4.0454
Py4	5.5955	3.8688
Py5	5.4660	3.7678
Py6	5.3928	3.7120
Py7	5.3182	3.6622
Py8	5.2796	3.6372
Py9	5.2423	3.6146
Py10	5.2159	3.5966

From Table 5, it can be seen that aluminum will act as a Lewis base while the inhibitors pyrrole oligomers act as a Lewis acids. So aluminum 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 $LUMO_{inh}$ – $HOMO_{Al}$ gap fall between 5 and 3 eV. Strong covalent bond can be expected only if $LUMO_{inh}$-$HOMO_{Al}$ gap is approximately zero eV [22].

It can be seen from Table4 . that aluminum will act as a Lewis acids while the inhibitors pyrrole oligomers act as a Lewis a base Table 6 . In this case, pyrrole oligomers act as anodic inhibitor.The Separation energy, $\Delta E_{gap} = (E_{LUMO} - E_{HOMO})$, is an important parameter Table 6. 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 [23]. The effectiveness of pyrrole oligomers as inhibitors has been further addressed by evaluating the global reactivity parameters such as the eleectronegativit (χ) ,the global chemical hardness (η), the global softness (σ) , the fraction of electrons transferred (ΔN), from the inhibitor to aluminum, and the electrophilicity, ω, are tabulated in Table6.

Table 6. Calculated quantum Chemical parameters for pyrrole oligomers and aluminum by DFT method.

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

ΔN	Ω
0.0850	0.6791
0.0870	1.0293
0.0897	1.2508
0.0912	1.4069
0.0919	1.5133
0.0921	1.5847
0.0922	1.6953
0.0921	1.6953
0.0921	1.7366
0.0921	1.7665

X_{Al}= 3.2093 , η_{Al}= 2.7764

The bonding tendencies of the inhibitors towards the metal atom can be discussed in terms of the HSAB (Hard –Soft – Acid – Base) and the frontier-controlled interaction concepts [24, 25]. General rule suggested by the principle of HSAB, is that hard acids prefer to co-ordinate to hard bases and soft acids prefer to co-ordinate to soft bases. On the other hand, metal atoms are known as soft acids[26]. Hard molecules have a high HOMO-LUMO gap and soft molecules have a small HOMO-LUMO gap [27]. And thus soft bases inhibitors are the most effective for metals [28]. So pyrrole oligomers which have the lowest energy gap and the highest softness have the most inhibitor efficiency this could also be confirmed by calculating another quantum chemical parameter (σ),which measures the softness of the molecule and so its reactivity. the number of electrons transferred (ΔN) was also calculated and tabulated in Table 6. Values of (ΔN) show the inhibition efficiency resulting from electron donation by inhibitor to aluminum [29]. The inhibition efficiency increases by increasing electron-donating ability of these inhibitors to donate electrons to the metal, the highest fraction of electrons transferred is associated with the best inhibitor. The electrophilicity index,(ω), shows the ability of the inhibitor molecules to accept electrons. The Values of (ω) were found to increase as the number of pyrrole molecules increases, suggesting an increase in the ability of the pyrrole oligomers to accept electrons from aluminum. The effectiveness of pyrrole oligomers under investigation has been further addressed by evaluating the global reactivity parameters are tabulated in Table 6. It can be seen that an increase in both ΔN (donation of electrons) and ω (back donation) values result from the increase in the number of pyrrole molecules. These donation and back–donation processes strengthens the adsorption of pyrrole oligomers onto the aluminum surface and increase the inhibition efficiency.

CONCLUSIONS

The present theoretical study indicates the following facts or observations:

In the case of aluminum interaction with the pyrrole oligomers, it was found that the ionic interaction character even more pronounced, because the values of (E_{LUMOAl}-$E_{HOMOinh}$) gap fall between 5 and 3 eV by DFT calculations. This suggests that the pyrrole oligomers act as good inhibitor for aluminum. Again DFT calculations show a better ionic interaction of aluminum with the pyrrole oligomers as compared to PM3 calculations. interaction by increasing in the number of pyrrole molecules.

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