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Theoretical Studies of Corrosion Inhibition of Coumarin and Coumarin Derivative on Iron by Density Functional Theory Approaches

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Abstract: *Corrosion of iron is a persistent problem that affects its structural integrity and durability in various industrial applications. The design of effective corrosion inhibitors is crucial for mitigating iron corrosion. In recent years, coumarin derivatives have shown promising potential as corrosion inhibitors for iron due to their distintive chemical properties. In this research, we employ density functional theory (DFT) calculations to investigate electrochemical parameters of coumarin derivatives on iron corrosion. Coumarin (a) and its derivative: hymechromone (b), esculetin (c), and scopoletin (d) are analyzed using DFT calculation. Some descriptors are applied to identify such as ionisation energy (I), electron affinity (A),* E_{HOMO}, E_{LUMO}, ΔE_{gap}, *electronegativity* (χ), *hardness* (η), *number of fraction electron transferred* (ΔN). *Based on the* ΔN *parameter the order of potential compounds that have potential inhibitors is* $c > b > d > a$. *The presences of electron donating groups in coumarin structure will increase the potency of efficiency inhibition of coumarin*

Keywords: *corrosion, coumarin, DFT, electronegativity, hardness, electron transferred.*

INTRODUCTION

Corrosion, the deterioration of materials due to chemical or electrochemical reactions with their environment, is a global issue affecting numerous industries. The economic impact of corrosion is substantial, with estimated costs reaching several percent of a country's gross domestic product (GDP) (Javaherdashti, 2000) According to research, indirect costs typically equal direct expenses, meaning that the total cost of corrosion may exceed 6.2% of world GDP. The World Bank estimates that the global GDP for 2021 will be roughly 96.1 trillion US dollars, with a cost of corrosion of about 6 trillion US dollars (Iannuzzi & Frankel, 2022). Corrosion that occurs in iron there are magnetite (Fe_3O_4) in the inner layer and lepidocrocite (γ-FeOOH) in the outer layer. Corrosion of iron occurs at a slow pace, but once corrosion has begun, the deterioration process of iron will occur rapidly. Corrosion of iron can occur at humidity above 60 percent. Corrosion of iron occurs at a slow pace, but once corrosion has begun, the deterioration process of iron will occur rapidly (Megahed et al., 2021). Therefore, the development of efficient corrosion inhibitors is utmost importance to mitigate iron corrosion and enhance its durability.

In recent years, organic compounds have gained attention as corrosion inhibitors due to their versatility, low toxicity, and potential for chemical modifications. (A. A. Al-Amiery et al., 2023). Among these compounds, coumarin derivatives have emerged as promising candidates for corrosion inhibition for iron. Coumarin derivatives are a class of compounds characterized by a benzene ring fused with an α-pyrone ring, exhibiting diverse biological activities such as antimicrobial, antioxidant, and anticancer properties. By

leveraging their inherent chemical reactivity and structural flexibility, coumarin derivatives hold promise for inhibiting corrosion and protecting metal surfaces from degradation (Mahalakshmi et al., 2021; Verma et al., 2021a). By harnessing their distinctive chemical properties, designing and developing novel coumarin-based compounds with enhanced corrosion inhibition capabilities is possible.

Quantum chemical calculations have obtained extensive utilization in examining reaction mechanisms and have demonstrated their remarkable efficacy in investigating inhibition mechanisms. These studies have delved into exploring the connection between structural parameters, including electronic properties of inhibitors, frontier molecular orbital energies (E_{HOMO}, E_{LUMO}), the charge distribution of the inhibitors under investigation, and their corresponding inhibition efficiencies (Wang et al., 2006). Density Functional Theory (DFT) has proven to be an invaluable tool for investigating the electronic properties of corrosion inhibitor compounds (Mecibah et al., n.d.). DFT calculations allow exploring the inhibitive properties of coumarin derivatives correlate to their molecular structure, providing insights into their quantum chemical parameters. By comprehending the fundamental principles of quantum chemical parameters and their corresponding inhibition efficiency between coumarin derivatives and metal substrates, researchers can design and develop novel inhibitors with enhanced corrosion protection capabilities.

Several studies have been conducted to investigate the corrosion inhibition properties of coumarin derivatives, specifically targeting iron substrates. Verma's research group found that the use of coumarin derivatives named 3-(3-benzyl-4-hydroxy-2-thioxo-3,4-dihydro-2H-1,3-thiazin-6-yl)-8-methoxy-2H-chromen-2-one (**BTMC**) and 3-(3-benzyl-4-hydroxy-2-thioxo-3,4-dihydro-2H-1,3-thiazin-6-yl)-2H-chromen-2-one (**BTC**) have been synthesized and applied as corrosion inhibitors with inhibition efficiency (EI) of 93.59% and 92.17% for BTMC and BTC against mild steel (Verma et al., 2021b). Al-amiery group also reported that 3-(5-amino-1,3,4-thiadiazole-2-yl)-2H-chromen-2-one (3-ATC) and 2-(coumarin-4-yloxy)-acetohydrazide (EFCI) can used as mild steel corrosion inhibitor with IE of 96% (3-ATC) and 94.7% (EFCI) (A. Al-Amiery et al., 2014; Al-Azzawi et al., 2023). Experimental investigations have employed various techniques to evaluate the effectivity of coumarin derivatives in mitigating metal corrosion. Some research evaluated the corrosion inhibition performance of coumarin derivatives compounds on aluminum alloy using various electrochemical measurements and confirmed their significant protective effects (Mohamad et al., 2014). In addition to experimental studies, computational investigations have hold a vital role in understanding the underlying mechanisms of coumarin as a corrosion inhibitor for iron. A study investigated coumarin's adsorption mechanism and corrosion inhibition effect as a green inhibitor. Computational studies have provided valuable insights into adsorption models by assessing frontier orbital parameters, and adsorption configurations have been acquired from quantum chemical calculations and molecular dynamics simulations of coumarin derivatives. Furthermore, the role of different concentrations in enhancing the corrosion inhibition efficiency of coumarin derivatives (Tang et al., 2021).

This research aims to explore the potential activity by utilizing DFT calculations of various coumarin derivatives as corrosion inhibitors correlate to their molecular structure and their corresponding corrosion-inhibiting effect for iron basen on the fraction of electrons transfer (ΔN). This research will contribute to the design and development of efficient coumarin-based inhibitors with improved performance for corrosion protection.

RESEARCH METHODS

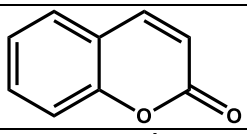
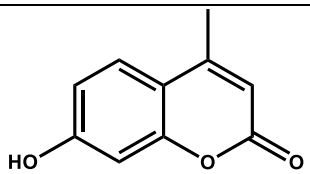
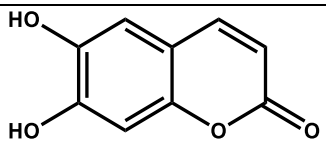
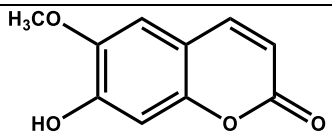
Materials and Tools

This study was conducted using Laptop with processor Intel® Core™ i5-7200U, CPU @2.5 GHz, and 8Gb RAM. The calculation conducted through Orca 4.2.1 for calculation and Avogadro for drawing structure of organic compound, and IboView to interpret HOMO-LUMO.

Procedures

The quantum chemical calculation was performed using Orca 4.2.1. The optimum geometry was downloaded from PubChem (https://pubchem.ncbi.nlm.nih.gov/). The computational calculation using density functional theory (DFT) with basis set def2-TZVP. The structure of the coumarin and coumarin derivatives is available table 1.

Table 1. Structure of coumarin derivatives

No	Compound	Structure
A	Coumarin	
B	Hymecromon	
C	Esculetin	
D	Scopoletin	

The quantum decriptor like energy of the highest occupied molecular orbital (E_{HOMO}), the energy of lowest unoccupied molecular orbitals (E_{LUMO}), energy gap (ΔE_{gap}), electronegatifity (χ), hardness (η) and softness (σ) were calculated.

Electronegativity (χ) is the tendency of a group or atom to attract electrons to itself when an atom or group combined with another atom. According to DFT it can be expressed with equation below. (Shahraki et al., 2016; Yadav et al., 2014).

$$\chi = -\left(\frac{\partial \mathrm{E}}{\partial \mathrm{N}}\right)_{v(r)} \quad \ldots (1)$$

E is the electronic energy in electron voltts, N is the number of electrons, $v(r)$is the external potential generated by the nuclei. However, using deffinite method, the equation 1 can be calculated as follows (Shahraki et al., 2016):

$$\chi = \frac{I + A}{2} \dots (2)$$

where I is negative value of E_{HOMO} and A is negative E_{LUMO}.

$$I = -E_{HOMO} \dots (3)$$

$$A = -E_{LUMO} \dots (4)$$

The hardness of molecule (η) exhibits the resistance of an atom to transfer charge related to the energy gap between the LUMO energy and the HOMO energy. The hardness of the molecules can be calculated using equation (5).

$$\eta = \frac{I - A}{2} \dots (5)$$

the amount of transferred charge (ΔN) from inhibitor to surface of metal was calculated by equation (6) based on the Pearson method (Guo et al., 2017).

$$\Delta N = \frac{(\chi_M - \chi_{mol})}{2(\eta_M + \eta_{mol})} \dots (6)$$

In this study, χ_M and χ_{mol} is defined as absolute electronegativity of metal and electronegativity of inhibitor. Furthermore, η_M and η_{mol} are the absolute hardness of metal and inhibtor. In this research, absolute electronegativity (χ_M) of iron is 4.32 eV and 0 eV for hardness of Fe.

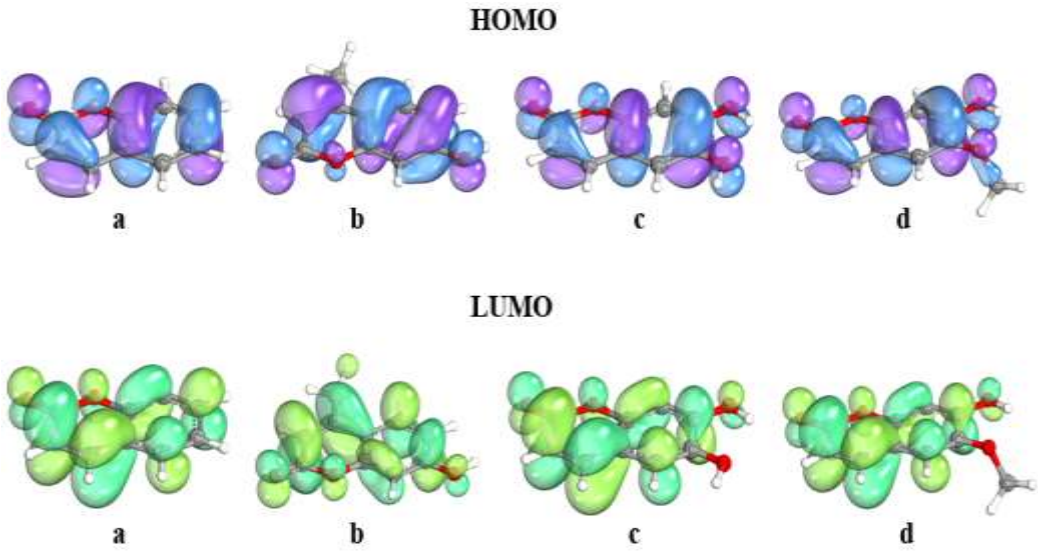
RESULTS AND DISCUSSION

The calculation results of E_{HOMO}, E_{LUMO}, and ΔE_{gap} are available in table 2. The global reactivity of coumarin and its derivatives is investigated through frontier molecular orbital involve energy of HOMO (highest occupied molecular orbitals) level and LUMO (lowest unoccupied molecular orbitals) level of chemical species. This relationship of band gap was discovered by Fukui (Fukui, 1982; Fukui et al., 1952). The energy level of HOMO (E_{HOMO}) is often related to the electron-donating ability of a chemical species. Previous experiments suggested that adsorption from inhibitors to metal surfaces could occur due to interactions between pi-electrons of heterocyclic compounds and empty orbitals on metal surface. Otherwise, energy level of LUMO (E_{LUMO}) represents the ability of molecules to accept electron atoms (Ebenso et al., 2010).

Table 2. Quantum parameter of coumarin and coumarin derivatives calculated at B3LYP with basis set def2-TZVP.

Parameter	Compound			
	a	**b**	**c**	**d**
E_{HOMO} (eV)	-6.849	-6.435	-6.220	-6.394
E_{LUMO} (eV)	-2.090	-1.769	-1.916	-1.886
ΔE_{gap} (eV)	4.759	4.667	4.305	4.509

The high value of E_{HOMO} levels tends to donate electron to low energy species. Increasing of E_{HOMO} values affect the inhibitory ability of an inhibitor. This is due to the influence of the transport process to the metal surface. The adsorption of inhibitor to the metal surface is linearly proportional to the value of E_{HOMO} (Khalil et al., 2016; Wazzan, 2015). From the calculated data in table 2, the order E_{HOMO} is **c > d > b > a**, In general, the lower value of ΔE_{gap} will increase the inhibition potency because the energy to lose an electron in the last occupied orbital will be low.



. **Figure 1**. Frontier molecular orbital diagram of coumarin and its derivatives.

Figure 1 exhibits the HOMO and LUMO of the coumarin and its derivatives in this study. Based on those HOMO and LUMO orbital, compound **a**, **b**, **c**, and **d** exhibit a contribution of *p*-orbitals in the benzene ring on the HOMO and LUMO.

The other important parameters of quantum calculation are ionization potential (I), electron affinity (A), electronegativity (χ), hardness (η), and electron transferred (ΔN). All these parameters are available in table 3.

Table 3. Quantum parameter calculations of coumarin and its derivatives

Parameter	Compound			
	A	**b**	**c**	**d**
I (eV)	6.849	6.435	6.220	6.394
A (eV)	2.090	1.769	1.916	1.886
χ (eV)	4.469	4.102	4.068	4.140
η (eV)	2.380	2.333	2.152	2.254
ΔN (eV)	0.074	0.154	0.175	0.151

According to Koopman's theorem, ionization energy and electron affinity of molecules are approximately proportional to the negatives value of E_{HOMO} and E_{LUMO} (Fiala et al., 2019). Ionization energy and electron affinity can be calculatd using equation 3 and equation 4. Electronegativity (χ) is a tendency of atom or group to attract electron toward it. The electron will partially move from lower electronegativity to higher electronegativity. A good inhibitor can easily transfer electrons to the metal surface. Therefore, a decent inhibitor will have a low electronegativity value. According to table 3, the order of electronegativity of coumarin and its derivative are **c < d < b < a**.

Chemical hardness is defined as the resistance to polarization or deformation of the electron cloud of molecules (Kaya & Kaya, 2015). Based on Pearson's principle about hard-soft-acid-base (HSAB), metals are considered to hard acid. In other hand, the inhibitor of corrosion act as soft bases. According to HSAB, the most effective inhibitor will be a delicate compounds (has lower hardness value) (Khalil et al., 2016; Saha et al., 2018) . Table 3 reveals the order of hardness value of coumarin, and its derivative are **c < d < b < a**. Based on the Principle of Maximum Hardness (PMH), a chemical system can be arranged to achieve the maximum hardness value. In other words, molecules that have a high hardness value have a low effectivity of corrosion inhibitor efficiency (Obot et al., 2016).

In corrosion inhibitor systems, iron (metal) and inhibitors, are brough together, so electrons will flow from high electronegativity (inhibitor) to low electronegativity (metal). Furthermore, the number of fractions of electrons transferred (ΔN) can be calculated using the equation 6. A negative value of ΔN indicates that a compound tends to act as acceptor electrons, meanwhile a positive value of ΔN indicates the tendency of molecules to act as donor electrons (Lgaz et al., 2017; Saha et al., 2015, 2018). The value of ΔN is tabulated in table 3. In this study, coumarin and its derivatives have a positive ΔN value so it can be said that coumarin and its derivatives have properties as electron donors in this system. A high ΔN value indicates a tendency for the inhibitor to interact with metal surfaces more easily, so the ΔN value has an influence on the efficiency of inhibition. Molecules that have a high ΔN value will have better potential as inhibitors than molecules with a lower ΔN (Chen et al., 2021). The value of ΔN is affected by several parameters, such as hardness, electronegativity, and energy gap. According to table 3, molecule **c** has higher value of fraction of electrons transfer, and in turn, is **b, d, a**. Therefore, the efficiency inhibition order for molecules is **c > b > d > a.** Based on the value of ΔN and the molecular structure, the presence of electron-donating groups such as -OH (hydroxy), -OR (alkoxy), and methyl will affect the electron-donating properties of the inhibitor molecule (Hadisaputra et al., 2019). The ΔN value for molecule **c** is larger than the other molecules due to the presence of two hydroxy groups, while compound **a** does not have electron donating groups in its ring system, so it has a smaller ΔN value than the others. The study of molecular structure and inhibition potency using DFT calculation is important to be in charge as reference study

for future research to develop coumarin-based molecular structures as corrosion inhibitors, this study examines the impact of the molecular structure of coumarin derivatives.

CONCLUSIONS

DFT calculations of coumarin and its three derivatives as corrosion inhibitors had been carried out. Based on theoretical studies conducted, coumarin and its derivatives have the potential as electron donors for corrosion inhibitors. Quantum calculation descriptors as corrosion inhibitors include E_{HOMO}, E_{LUMO}, ΔE_{gap}, electronegativity (χ), hardness (η), and transfer charge (ΔN). Based on the ΔN parameter the order of potential compounds that have potential inhibitors is **c > b > d > a**. The presences of electron donating groups like -OH (hydroxy), -OR (alkoxy), in coumarin structure will increase the potency of efficiency inhibition of coumarin.

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