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4 ***Ab initio*MP2 and DFT studies of ethyl-p-methoxycinnamate and its derivatives as corrosion inhibitors of iron in acidic medium**

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Abstract. The efficiency of ethyl-p-methoxycinnamate(EPE) and its derivatives as corrosion inhibitors of iron in acid environment has been studied to find the relationship between molecular structure and electronic parameters with their efficiency of corrosion inhibition. The *ab initio* MP2 perturbation theory and DFT method were applied to calculate molecular structure and electronic parameters of inhibitors. Computational and experimental corrosion inhibition efficiency show that the electronic properties of molecules, including the orbital molecular frontier energy (HOMO and LUMO energy), ionization potential, electron affinity, electronegativity, number of electron transfer from inhibitor to metal and interaction energy have a strong relationship with inhibition performance. Interaction mechanism obtained from natural bond orbital analysis was employed to study the interactions between inhibitors with iron metal in more detail. The presence of electron donor groups within the frameworks of inhibitors has a less significant effect compared to π -electron contribution on corrosion inhibition performance.

1. Introduction

At present the development of natural product based corrosion inhibitors is still intensively developed. These type of inhibitors are favoured due to they are inexpensive, biodegradable, environmentally friendly and non-toxic. In addition, these inhibitors can be easily obtained from abundant natural products [1-4]. Natural product compounds consist of atoms (N, O, P, and S) which have free electron pairs as electron donors and π type electrons to facilitate the formation of complexes with metals [5,6]. An example of a potential corrosion inhibitor of natural products is ethyl-p-methoxycinnamic (EPE). Pure EPE compound can be obtained from isolating sand ginger (*kaempferia galanga*). Sand ginger plants grow widely in Indonesia and many parts of Southeast Asia. They are commonly used as traditional medicine, cooking spices, cosmetics and drinks. The pure compound of EPE can be isolated using several techniques [7-9]. Structurally, ethyl-p-methoxycinnamic consists of methoxy groups, esters and conjugated double bonds in the benzene ring. These three functional groups are electron donors which facilitate bonding with metal surfaces.



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Recently, pure EPE have been tested to prevent iron corrosion in 1 M HCl using weight loss, electrochemical impedance spectroscopy [10]. EPE shown to be effective in inhibiting iron corrosion in 1M HCl. Increased EPE concentration can reduce the corrosion rate of iron in 1M HCl. The mechanism of inhibition is exothermic, spontaneous, and follows the isothermal adsorption mechanism by forming multilayer EPE on the iron surface. Thermodynamic studies with E_a values < 80 kJ and $\Delta G^{\circ}_{ads} < -20$ kJ/mol indicate the inhibition processes is spontaneous and exothermic. However, experimental studies have not been able to explain in detail the mechanism of interaction between EPE and ferrous metals. The use of MP2 and DFT methods can principally be used to overcome the problem. Theoretical study is able to accurately predict structural parameters in which structure parameters can be used to determine the mechanism of interaction between metal inhibitors [11]. In addition, the theoretical approach is able to predict the electronic parameters related to the interaction mechanism [12-15]. The studied electronic parameters are frontier molecular orbital, ionization potential, electron affinity, electronegativity, number of electron transfer from inhibitor to metal, and interaction energy. In addition, we present the interaction mechanism from the natural bond orbital analysis.

2. Method

The MP2 and DFT method was used for geometry optimization and a single point energy calculation from EPE. All quantum parameters are calculated using the Gaussian 09 package [16]. The LanL2DZ with effective core potential and 6-31G(d) were applied as basis sets for iron and EPE, respectively. Corrosion occurred in aqueous medium, so a single point energy calculation was carried out using a PCM method to mimic the corrosion conditions in the aqueous environment. Re-optimization of EPE structure in the aqueous phase was not carried out because it has a minor effect on the energetic [10, 17-22].

3. Result and discussion

Geometry parameters are important to explain the accuracy of the calculation method. In addition, geometry parameters can be used as an initial reference for the mechanism of interaction between EPE and iron. Figure 1 shows the optimized structure of EPE compounds and derivatives. The comparison of the geometry parameters between experimental and theoretical MP2/DFT is depicted in Table 1. It shows that a relatively small difference in distance and binding angle between experimental and theoretical studies with an average of 0.018 \AA and 0.773° . The suitability of the theoretical structure parameters with the experiment indicates that the MP2 and DFT methods with LanL2DZ and 6-31G(d) basis function combination are well-accurate. The addition of electron donating (NH_2) and electron withdrawing (NO_2) groups was carried out to predict the substituent effect on EPE corrosion efficiency. Figure 1 indicates that there is no significant structural change to the addition of electron denoting-withdrawing groups. The lack of structural changes leads to predictions that π aromatic electrons in benzene rings contribute higher than the substituent for the interaction of metal and inhibitor.

The quantum descriptor parameter can be used to predict the inhibitor efficiency theoretically (IEtheory.%). Quantum electronic parameters such as ionization potential, electron affinity, electronegativity, electron transfer are obtained from HOMO and LUMO energy [10]. The difference between the energy of HOMO and LUMO is the value of the energy gap. The large energy gap (E_{gab}) describes the molecule as having high stability, while its activity is weak. It is depicted from Table 2 that EPE- NH_2 has the lowest E_{gab} so that EPE- NH_2 has the highest inhibitory performance. For charge transfer capability, EPE- NH_2 has the highest ability to donate electrons ΔN so that it can be predicted that it has the highest inhibitory ability. Based on quantum parameters, the order of IE% values is EPE- $\text{NH}_2 > \text{EPE} > \text{EPE-NO}_2$.

Table 1. Comparison of geometrical parameters of EPE between experimental and theoretical calculation.

Bond Length	Exp* (Å)	DFT (Å)	MP2 (Å)	Bond Angle	Exp* (Å)	DFT (Å)	MP2 (Å)
C1-O1	1.368	1.361	1.365	O1-C1-C2	124.2	118.5	125.1
C1-C2	1.381	1.404	1.408	O1-C1-C6	115.5	115.7	115.5
C1-C6	1.381	1.411	1.408	C2-C1-C6	120.3	119.5	119.4
O1-C12	1.420	1.419	1.420	O1-C1-C12	118.5	118.5	116.4
C2-C3	1.392	1.399	1.405	C1-C2-C3	118.7	119.3	119.4
C3-C4	1.382	1.407	1.410	C2-C3-C4	122.1	122.0	121.9
C4-C5	1.394	1.417	1.418	C3-C4-C5	117.7	117.4	117.8
C4-C7	1.471	1.461	1.467	C3-C4-C7	119.3	119.0	118.8
C5-C6	1.377	1.387	1.394	C5-C4-C7	122.9	123.4	123.4
C7-C8	1.319	1.352	1.357	C4-C5-C6	121.0	121.2	120.9
C8-C9	1.475	1.478	1.486	C1-C6-C5	120.2	120.3	120.6
C9-O9 ₍₁₎	1.201	1.220	1.222	C4-C7-C8	127.7	127.7	126.9
C9-O9 ₍₂₎	1.335	1.359	1.358	C7-C8-C9	120.6	120.1	119.6
O9 ₍₂₎ -C10	1.458	1.441	1.441	C8-C9-O9 ₍₁₎	124.9	126.2	126.2
C10-C11	1.479	1.518	1.516	C8-C9-O9 ₍₂₎	111.5	110.5	110.1

*(Luger [23])

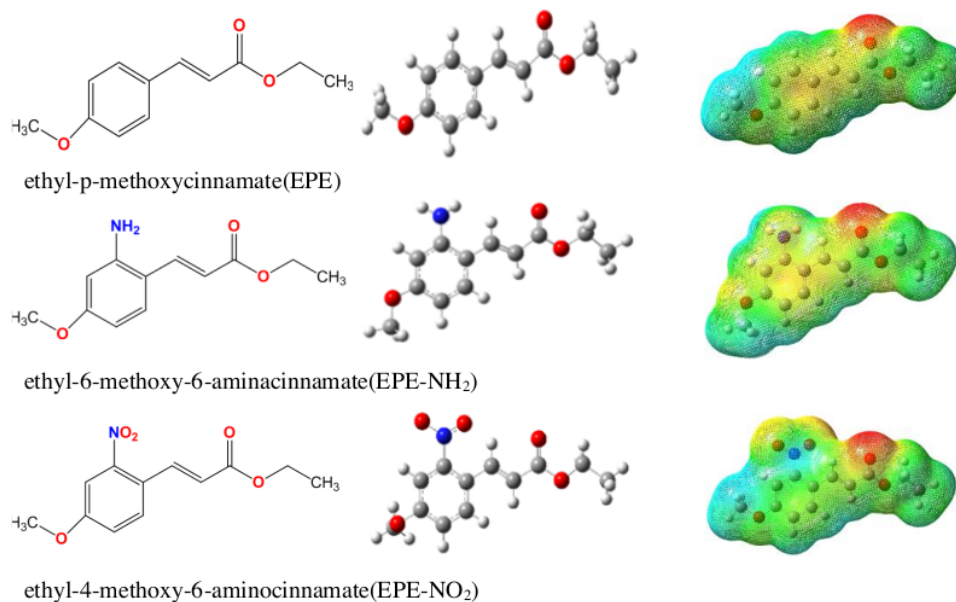


Figure 1. 2D, optimized structure and EPS of EPE and its derivate.

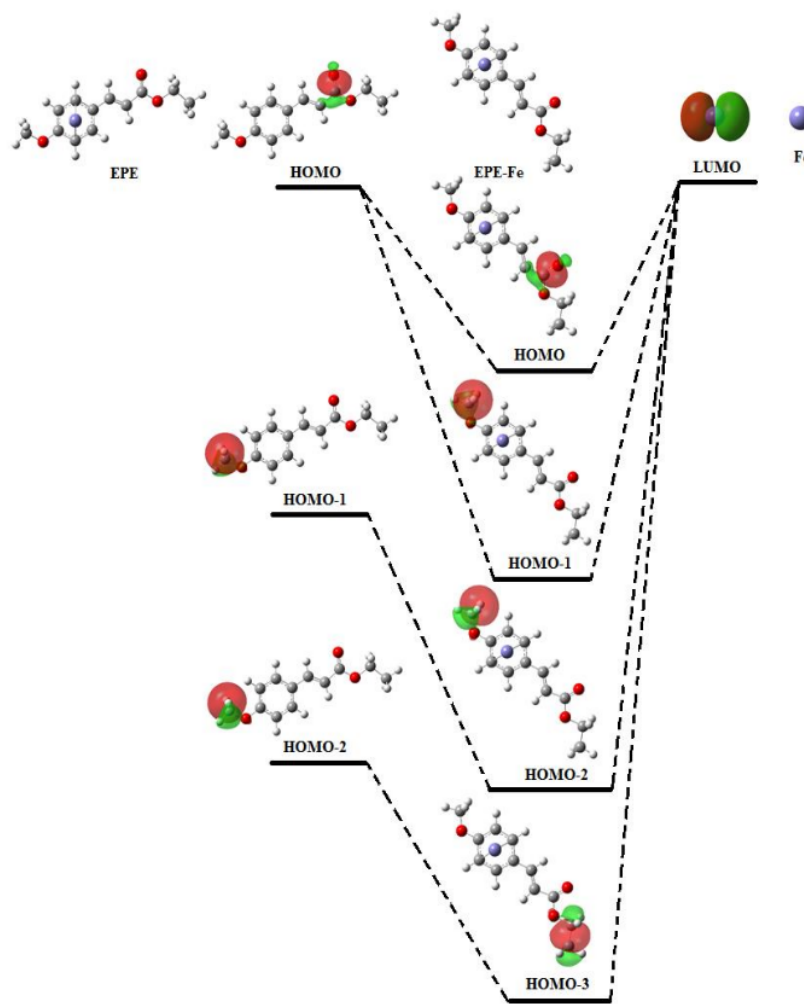


Figure 2. Interaction of molecular orbital EPE with Fe.

The strength of the interaction between the ligand (electron donor) and iron (electron acceptor) also depends on the interaction energy (ΔE). The amount of the interaction energy is closely related to the stability of the complex formed. Strong and stable interactions have low energy interactions. So the more negative ΔE , the more stable the interaction between the ligand and the metal. Table 2 shows that EPE-NH₂ shows the most stable interaction. This indicates that EPE-NH₂ compounds are better corrosion inhibitors compared to other EPE derivatives. The NH₂ substituent is a good electron donor group so it can donate more electrons to interact more strongly with metals. Other findings show that based on potential electrostatic visualization (ESP), it appears that the electronegativity is large in yellow in the EPE benzene ring area (Figure 1). The π electrons which are conjugated in the benzene ring will contribute more in interaction than substituent group.

Table 2. The quantum chemical parameters, corrosion inhibitor efficiencies and binding energies of the EPE and its derivatives obtained from B3LYP and MP2at 6-31G(d)level of theory

Parameters	EPE		EPE-NH ₂		EPE-NO ₂	
	DFT	MP2	DFT	MP2	DFT	MP2
E _{HOMO} (eV)	- 6.0635	- 6.7607	- 5.6867	- 5.5441	- 6.5362	- 6.0341
E _{LUMO} (eV)	- 1.8964	0.8988	- 1.8357	0.8800	- 2.9715	0.5385
E _{gab} (eV)	- 4.1672	- 7.6595	- 3.8510	- 6.4241	- 3.5647	- 6.5726
I (eV)	6.0635	5.7607	5.6867	5.5441	6.5362	6.0341
A (eV)	1.8964	- 0.8988	1.8357	-0.8800	2.9715	- 0.5385
χ (eV)	3.9799	2.9309	3.7612	2.3320	4.7538	2.7478
ΔN	0.7247	0.5312	0.8411	0.7266	0.6301	0.6470
IEtheory%	76.2276	74.3334	80.4611	82.4576	69.7064	71.9450
ΔE (kJ.mol ⁻¹)	-165.95	-166.85	-175.56	176.65	-170.46	-171.32

The mechanism of interaction between EPE and iron can be seen in Figure 2. The interaction involves HOMO and HOMO1 orbital from EPE with iron orbital LUMO. It appears that the orbital in HOMO1 are also strongly involved in interaction. It indicates that there is an interaction between the sigma bonding orbital in EPE interacting with iron sigma antibonding. In addition, the possibility of back donation from the d orbital is pushed to the iron to the antibonding sigma of EPE. The detail of interaction can be seen from the results of the NBO analysis which will be presented in the next article.

Conclusion

A theoretical study has been carried out using MP2 and DFT/6-31G method to study the interaction mechanism between EPE and iron in term of corrosion inhibition. The calculation results show that quantum parameters have a good correlation with corrosion inhibition efficiency. The interaction mechanism also involves HOMO1 in addition to the HOMO orbital from EPE. Furthermore, it appears that the efficiency of corrosion inhibition increases due to the addition of electron donor substituent NH₂.

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