

## Corrosion Inhibition of Steel in Acidic Medium by Eugenol Derivatives: Insight from Density Functional Calculation

Saprizal Hadisaputra\*, Saprini Hamdiani, and Agus Abhi Purwoko

Department of Chemistry Education, Faculty of Science and Education, Mataram University. Jalan Majapahit 62, Mataram, 83251, INDONESIA

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### ABSTRACT

Corrosion inhibition properties of eugenol derivatives have been elucidated by means of density functional theory at B3LYP/ 6-31G(d) level of theory. The quantum chemical parameters including the highest occupied molecular orbital ( $E_{\text{HOMO}}$ ) and lowest unoccupied molecular orbital ( $E_{\text{LUMO}}$ ), gap energy ( $\Delta E_{\text{gap}}$ ), ionization potential ( $I$ ), electron affinity ( $A$ ), the absolute electronegativity ( $\chi$ ), hardness ( $\eta$ ), softness ( $\sigma$ ), and the fraction of electron transferred ( $\Delta N$ ) are studied for investigating the corrosion inhibition performance of acetyeugenol derivatives. Effect of electron donating and withdrawing groups has been studied on the corrosion inhibition performance of acetyeugenol derivatives. The  $\text{NH}_2$  (electron donating substituent) exhibits the highest inhibition efficiency, whereas the  $\text{NO}_2$  (electron withdrawing substituent) exhibits the lowest inhibition efficiency. This study would have a significant contribution in designing highly potential eugenol based corrosion inhibitors.

**Keywords:** corrosion inhibitor, DFT method, eugenol, substituent.

\*Corresponding author: [rizal@unram.ac.id](mailto:rizal@unram.ac.id), Tel/Fax (+62)87738066422

### 1. Introduction

Eugenol is obtained from clove plant which is native to Indonesia. A part of being the biggest consumer, Indonesia also supplies 75% (two thousand metric ton) of the world demand on eugenol, isoeugenol and methyl eugenol yearly. Eugenol is viscous yellowish liquid, slightly soluble in water and easily dissolved in organic solvents. Eugenol is widely applied in perfumery, manufacturing stabilizers, antioxidants for plastics rubbers, dentistry, anesthetics, analgesics, anti-inflammatory agents and flavoring agents and corrosion inhibitor.

Considerable effort has been devoted to studying the metallic corrosion inhibition properties of eugenol and its derivatives (Chaieb et al., 2005; Kinani et al., 2014). The experimental work investigated the effect of eugenol and its derivative (acetyeugenol) on the corrosion inhibition of steel in 1 M HCl solution (Chaieb et al., 2005). It was observed that the extracts reduce the corrosion rate of steel in 1 M HCl significantly. The acetyl substituent attached to the eugenol change the corrosion inhibition efficiency. The inhibition efficiencies were found to increase with eugenol and acetyeugenol extract concentrations and attained 80 % and 91 % at concentration of 0.173 g/L, respectively.

This implies that acetyeugenol is more active to the surface as compared to eugenol due to the presence of the carbonyl group.

Currently, intensive efforts to gain high-efficiency, facile and feasible use of the corrosion inhibitors still a very active research area. Moreover, with increased awareness of the importance of the green chemistry applications in term of environmental pollution and control, it becomes significantly important to search for less toxic, readily available in plenty and environment-friendly corrosion inhibitors. Eugenol and its derivatives are one of the main candidates for the green corrosion inhibitor. With the help of theoretical calculations, eugenol corrosion performance can be studied more accurately and in a relatively short time. Several theoretical studies show that the corrosion inhibition properties of organic compound toward metal surface can be obtained by fast and accurate quantum-chemistry investigations (Cruz et al., 2004; Hadisaputra et al., 2016; Kabanda et al., 2013; Khaled and Al-Qahtani, 2009; Li et al., 1999; Liu et al., 2011; Musa et al., 2010; Obot and Obi-Egbedi, 2010). In this work, we use quantum chemical calculations to study the corrosion performance of acetyeugenol derivatives, mainly studied the effect of substituent groups on their corrosion performance.

## 2. Material and Method

### 2.1. Materials

Acetylugenol derivatives, including electron donating and withdrawing substituent (NH<sub>2</sub>, OH, -CH<sub>3</sub>, -COOH, -F, -NO<sub>2</sub>) as depicted in scheme 1.

### 2.2. Method

All the density functional theory (DFT) calculations have been performed with Gaussian 03 suit of quantum chemistry code (Frisch et al., 2004). The complexes were optimized using DFT method at B3LYP/631G(d) level of calculation. The optimized structures in all cases corresponding to the minimum energy point of the potential energy surface because no imaginary frequencies were found. The corrosion inhibition efficiencies were calculated and it was defined as:

$$I_{add} \cdot \% = \frac{I_{AE} - I_{x-AE}}{I_{AE}} \times 100 \% \quad \dots\dots\dots 1$$

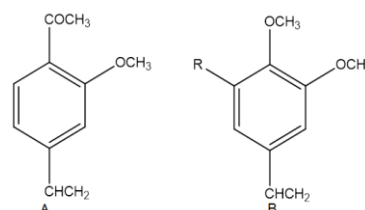
$$I_{eadd} \cdot \% = I_{add} \cdot \% - I_{eAE} \cdot \% \quad \dots\dots\dots 2$$

$$IE_{theor} \cdot \% = I_{eAE} \cdot \% + I_{eadd} \cdot \% \quad \dots\dots\dots 3$$

Where  $I_{add} \cdot \%$  is the percentage ionization potential of the substituted phenyl compounds,  $I_{eadd} \cdot \%$  is the inhibition efficiency % of the experimental compound, and  $IE_{theor} \cdot \%$  is the theoretically calculated percentage inhibition efficiency (Obayes et al., 2014). Corrosion dominantly occurs in the solution, therefore solvent effects were included using the PCM as implemented in the default Gaussian code using a dielectric constant of 78.4 for water. Structure reoptimizations in the presence of the solvent were found to have a minor influence on energetics (Hadisaputra et al., 2012, 2014b, 2014a). Therefore, the single-point approach has been employed in this study, as it allows computational costs to be minimized without sacrificing much accuracy in solvation energies.

## 3. Results and Discussion

In this study, two different types of the electron donating (R = -NH<sub>2</sub>, -OH, -CH<sub>3</sub>) and electron-withdrawing (R = -COOH, -F, -NO<sub>2</sub>) groups added to the framework of eugenol as shown in Scheme 1. The optimized structure of derivatives acetylugenol is shown in Figure 1. The optimized structures were obtained using Cs conformation.



**Scheme 1** Molecular structures of the studied acetylugenol (A) and the studied acetylugenol derivatives (B).

The frontier molecular orbitals related to the reactivity of the acetylugenol and its derivatives in gas and solvent phase are reported in Table 1 and Table 2. The interaction between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of reacting species lead to the transition of the electron within molecules. The transition of the electron in the form of electron donation and acceptance is measured by the energy value of molecular orbitals. The energy of the highest occupied molecular orbital ( $E_{HOMO}$ ) indicates the tendency of molecule towards the donation of the electron (Boda et al., 2012; Koopmans, 1934). The higher values of  $E_{HOMO}$  the higher the adsorption of the inhibitor on metal surfaces and therefore better inhibition efficiency. The energy of the lowest unoccupied molecular orbital ( $E_{LUMO}$ ) indicates the ability of the molecule to accept electron. The increasing HOMO and decreasing LUMO energy values relate to increasing binding ability

**Table 1.** Gas phase of the quantum-chemical parameters of acetylugenol (AE) and six models determined using DFT method at the B3LYP level

Compounds	$E_{HOMO}$ eV	$E_{LUMO}$ eV	$\Delta E_{gap}$ eV	$I$ eV	$A$ eV	$\chi$ eV	$\eta$ eV	$\sigma$ eV	$\Delta N$
AE	-6.1339	-0.3701	5.7639	6.1340	0.3701	3.2520	2.8820	0.3469	0.6502
AE-CH <sub>3</sub>	-6.0584	0.0001	6.0586	6.0585	-0.0001	3.0292	3.0293	0.3301	0.6554
AE-OH	-6.0768	-0.3015	5.7753	6.0768	0.3015	3.1892	2.8877	0.3463	0.6598
AE-NO <sub>2</sub>	-6.4991	-2.6186	3.8806	6.4992	2.6186	4.5589	1.9403	0.5153	0.6291
AE-NH <sub>2</sub>	-5.5383	-0.0634	5.4749	5.5383	0.0634	2.8009	2.7375	0.3653	0.7670
AE-F	-6.2608	-0.4180	5.8428	6.2608	0.4180	3.3394	2.9214	0.3423	0.6265
AE-COOH	-6.2678	-1.3889	4.8790	6.2679	1.3889	3.8284	2.4395	0.4099	0.6501

**Table 2.** Solvent phase of the quantum-chemical parameters of acetylugenol (AE) and six models determined using DFT method at the B3LYP level

Compounds	$E_{HOMO}$ eV	$E_{LUMO}$ eV	$\Delta E_{gap}$ eV	$I$ eV	$A$ eV	$\chi$ eV	$\eta$ eV	$\sigma$ eV	$\Delta N$
AE	-6.1176	-0.3439	5.7737	6.1176	0.3439	3.2308	2.8868	0.3463	0.6528
AE-CH <sub>3</sub>	-6.0081	-0.2794	5.7286	6.0081	0.2794	3.1437	2.8643	0.3491	0.6731
AE-OH	-6.1065	-0.2326	5.8738	6.1065	0.2326	3.1695	2.9369	0.3404	0.6521
AE-NO <sub>2</sub>	-6.6050	-2.3872	4.2177	6.6050	2.3872	4.4961	2.1088	0.4741	0.5936
AE-NH <sub>2</sub>	-5.4098	0.1872	5.5971	5.4098	-0.1872	2.6113	2.7985	0.3573	0.7840
AE-F	-6.2578	-0.4359	5.8218	6.2578	0.4359	3.3468	2.9109	0.3435	0.6274
AE-COOH	-6.2461	-1.3720	4.8741	6.2461	1.3719	3.8090	2.4370	0.4103	0.6546

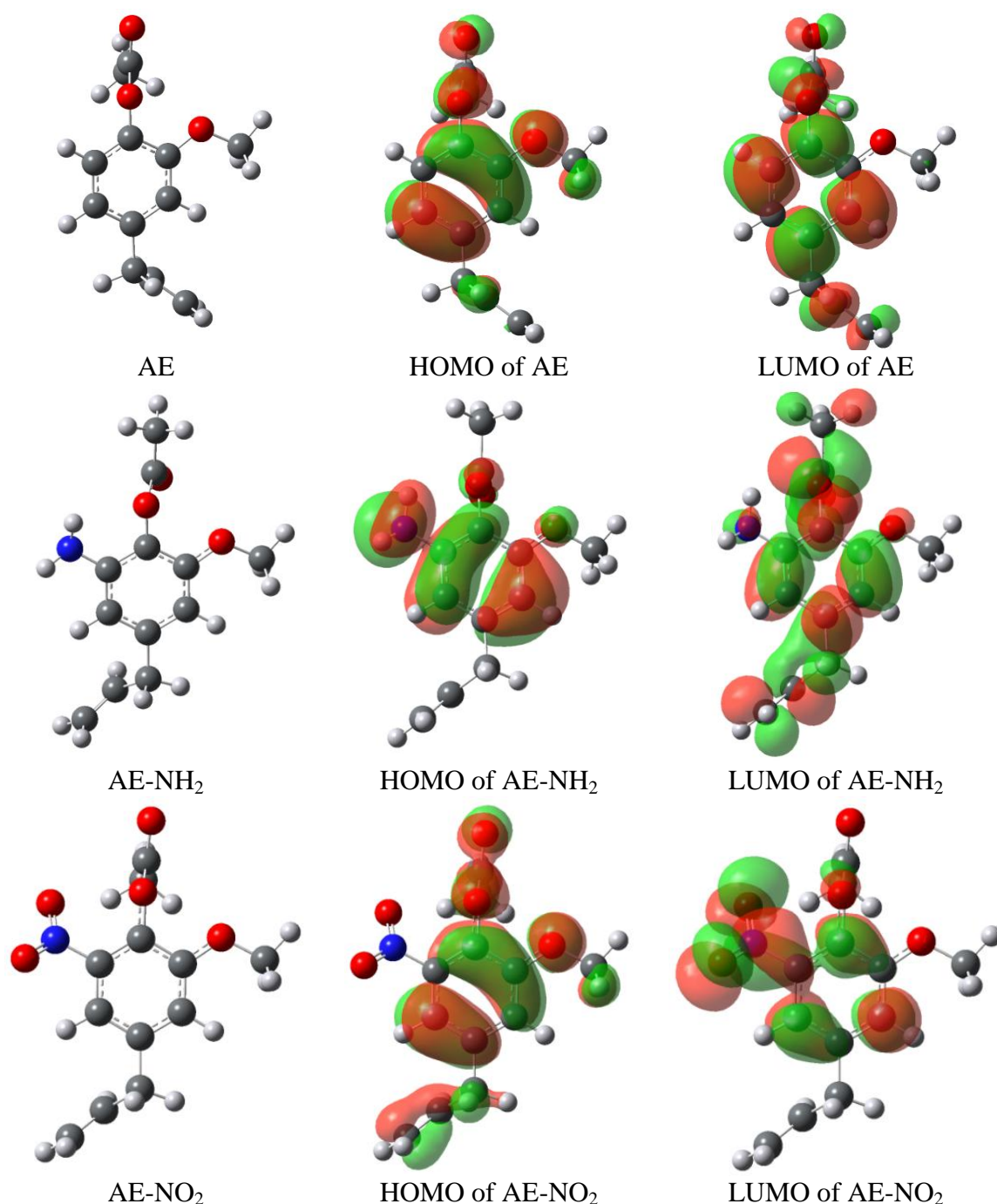


Fig. 1. Selected molecular orbitals, HOMO and LUMO of the studied AE, AE-NH<sub>2</sub> and AE-NO<sub>2</sub> using the DFT/B3LYP method

of the inhibitor to the metal surface.

From Table 1, it can be seen that the  $E_{\text{HOMO}}$  for the acetyleugenol and six compound models in gas phase follow the order of  $\text{NH}_2 > \text{CH}_3 > \text{OH} > \text{H} > \text{COOH} > \text{F} > \text{NO}_2$ . The  $E_{\text{HOMO}}$  value of AE-NH<sub>2</sub> is -5.4098 eV which is the highest value among other molecules, in contrast, the  $E_{\text{HOMO}}$  of AE-NO<sub>2</sub> -6.6050 eV exhibit the lowest  $E_{\text{HOMO}}$  value. It predicts that AE-NH<sub>2</sub> has the highest inhibition efficiency than the other compounds. Meanwhile, AE-NO<sub>2</sub> contributes to the lowest inhibition efficiency. The similar trend is also found in the solvent phase where the electron donating substituent increases the inhibitor efficiency and in contrast, the electron

withdrawing substituent reduces the inhibition efficiency.

In order to give a clear view of the frontier molecular orbitals, the visualization of molecular orbitals calculated by the DFT method is depicted in Fig. 1. It shows clearly that there are different in electron distribution between two selected compounds, AE-NH<sub>2</sub> and AE-NO<sub>2</sub>. The electron distribution of AE-NH<sub>2</sub> is concentrated in multiple  $\pi$  electrons of benzene, as a result, AE-NH<sub>2</sub> more capable of binding toward metal surfaces compared with AE-NO<sub>2</sub>. The electron distribution of AE-NO<sub>2</sub> spread out over the molecule so that it has lower capability toward metal surfaces.

Ionization can be used to describe the chemical reactivity of atoms and molecules. High ionization energy indicates high stability of atoms and molecules while low ionization energy indicates high reactivity of the atoms and molecules (Foresman and Frisch, 1996; Ghosh and Islam, 2011). Table 1 shows that the ionization energy trends follow the trend of HOMO energy. Generally, AE-NH<sub>2</sub> has lower ionization energy than that of AE-NO<sub>2</sub>. It can be seen from the ionization energy value of AE-NH<sub>2</sub> is 5.5383 eV which smaller than the ionization energy of AE-NO<sub>2</sub> 6.4992 eV and other studied molecules. It predicts that AE-NH<sub>2</sub> has the better inhibition efficiency than the other compounds. The gas phase ionization potential trend correlates positively with the solvent phase trend in which the electron donating substituent increases the inhibitor efficiency contrast, the electron and in withdrawing substituent gives opposite result.

Table 1 also shows the positive correlation between the quantum chemical parameters trend: the electronegativity trend follows the order of frontier molecular orbitals and ionization potential: NH<sub>2</sub> > CH<sub>3</sub> > OH > H > COOH > F > NO<sub>2</sub>. It is clearly seen that the electronegativity value of AE-NH<sub>2</sub> is 2.8009 eV which smaller than the electronegativity of

AE-COOH and AE-NO<sub>2</sub>, 3.8284 eV and 4.4961 eV respectively. The similar trend also found for solvent phase. According to Sanderson's electronegativity equalization principle (Sanderson, 1976), AE-NO<sub>2</sub> groups with a high electronegativity quickly reach equalization and hence low reactivity is expected which in turn indicates low inhibition efficiency. In contrast, AE-NH<sub>2</sub> with a low electronegativity and high reactivity which in turn indicates high inhibition efficiency. The numbers of electrons transferred ( $\Delta N$ ) was also presented in Table 1 and Table 2.

The  $\Delta N$  values agree with Lukovits's study (Lukovits et al., 2001). If  $\Delta N < 3.6$ , the inhibition efficiency increases by increasing electron-donating ability of these inhibitors to donate electrons to the metal surface. It increases in the following order: NH<sub>2</sub> > CH<sub>3</sub> > OH > H > COOH > F > NO<sub>2</sub>. The  $\Delta N$  values correlate positively with the inhibition efficiencies. Thus, the highest fraction of electrons transferred is associated with the best inhibitor (NH<sub>2</sub>), while the least fraction is associated with the inhibitor that has the least inhibition efficiency (NO<sub>2</sub>).

Table 2 depicted the calculated inhibition efficiency IE% acetylugenol (AE) and six models determined using DFT method at the B3LYP level. The results demonstrate

Table 3 Calculated inhibition efficiency IE<sub>theory</sub>% of acetylugenol (AE) and six models determined using DFT method at the B3LYP level.

Compounds	I <sub>add</sub> %		I <sub>e,add</sub> %		Theoretical IE <sub>theory</sub> %		IE <sub>exp</sub> %
	Gas	Solvent	Gas	Solvent	Gas	Solvent	
AE	0	0	0	0	91.0000	91.0000	91
AE-CH <sub>3</sub>	1.7906	1.2312	1.6295	1.1204	92.6295	92.1204	
AE-OH	0.1824	0.9316	0.1660	0.8477	91.1660	91.8478	
AE-NO <sub>2</sub>	-7.9664	-5.9530	-7.2630	-5.4175	83.7374	85.5825	
AE-NH <sub>2</sub>	11.5690	9.7108	10.5470	8.8367	101.547	99.8368	
AE-F	-2.2907	-2.0670	-2.3260	-1.8812	88.6738	89.1188	
AE-COOH	-2.0995	-2.1830	-2.1320	-1.9862	88.8681	89.0138	

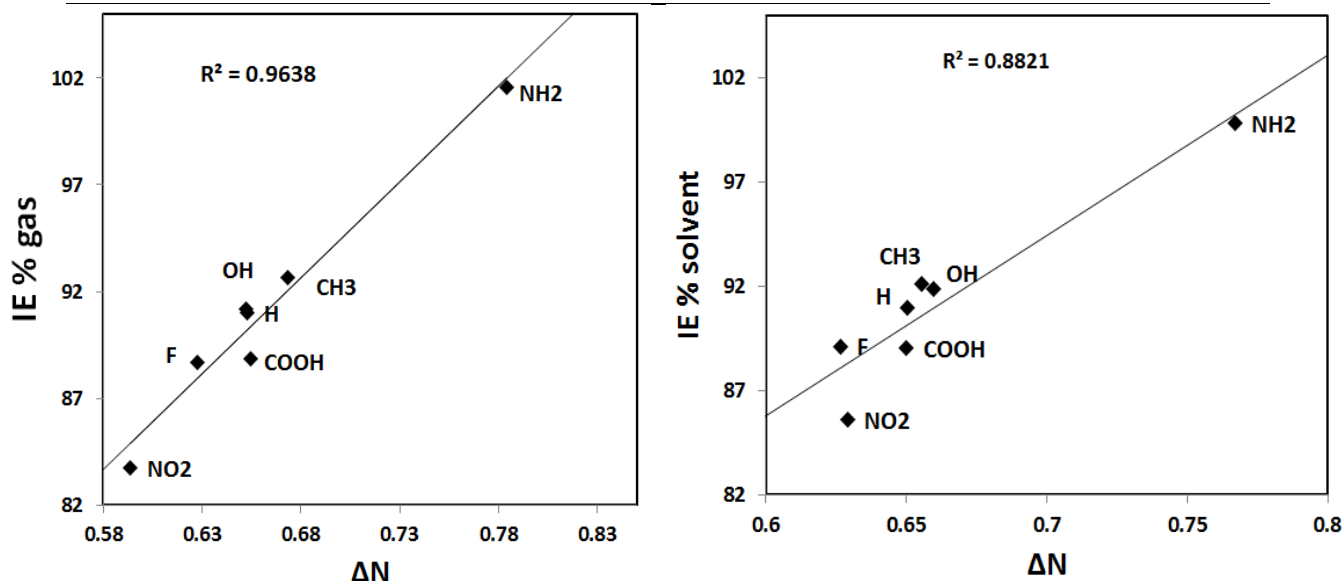


Fig. 2. Correlation between the number of electrons transferred ( $\Delta N$ ) and the corrosion inhibition efficiency (IE%) of acetylugenol (AE) and six models determined using DFT method at the B3LYP level.



that the addition of electron withdrawing nitro (NO<sub>2</sub>) substituent within the framework of acetyleneugenol lead to a decrease in inhibition efficiency. By contrast, the addition of electron donating amine (NH<sub>2</sub>) group led to an increase in inhibition efficiency. It is shown that the most efficient inhibitor was model AE-NH<sub>2</sub>, which displayed an inhibition efficiency of 99.83 % in solvent phase. The inhibition efficiency of AE was 91.00 % and it improves significantly with the addition of amine group. The correlation between the the number of electrons transferred ( $\Delta N$ ) and the corrosion inhibition efficiency is depicted in Figure 2. A good linear correlation has been identified between the number of electrons transferred ( $\Delta N$ ) and inhibition efficiencies for gas and solvent phase,  $r^2 = 0.9636$  and  $r^2 = 0.8821$ , respectively.

#### 4. Conclusion

A DFT study has been performed to study the corrosion inhibitor properties of acetyl eugenol (AE) and six AE derivatives. Quantum chemical parameters: the highest occupied molecular orbital ( $E_{\text{HOMO}}$ ) and lowest unoccupied molecular orbital ( $E_{\text{LUMO}}$ ), gap energy ( $\Delta E_{\text{gap}}$ ), ionization potential ( $I$ ), electron affinity ( $A$ ), the absolute electronegativity ( $\chi$ ), hardness ( $\eta$ ), softness ( $\sigma$ ), and the fraction of electron transferred ( $\Delta N$ ) calculated using DFT/B3LYP 6-31G(d) level of theory. The results demonstrate that the addition of electron donating substituent (NH<sub>2</sub>) exhibit the highest inhibition efficiency and the electron withdrawing substituent (NO<sub>2</sub>) exhibit the lowest inhibitor efficiency. The positive correlations are also depicted from quantum chemical parameters and inhibitor efficiency values. This theoretical approach would contribute to the design of new corrosion inhibitors with improved efficiency.

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