Theoretical study of copper corrosion prevention by terpenoid green inhibitors of thymol, carvacrol, and thymohydroquinone

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Abstract. Electronic parameters have been used to predict the corrosion inhibition performance of the green inhibitors of thymol, carvacrol, and thymohydroquinone against copper. Molecular modeling was carried out at the density functional and ab initio levels and Monte Carlo molecular dynamics. Tymohydroquinone can prevent copper corrosion better than the other two monoterpenoids. Molecular dynamics studies show that corrosion inhibitors are adsorbed on the metal surface, thereby inhibiting corrosion from occurring on the metal surface.

1 Introduction

Terpenoids are a large group of organic compounds found in various organisms, especially plants. Terpenoids have diverse biological functions and chemical properties and important roles in ecology, pharmaceuticals, and industry [1-4]. Essential oils containing terpenoids produce perfumes, cosmetics, and food [5-8]. Several terpenoids have potential health effects. Some have anti-inflammatory, antimicrobial, and antioxidant properties [9-10].
In addition, terpenoids can potentially be corrosion-inhibiting agents, especially in environments containing metals susceptible to corrosion [11-15]. These compounds may form a protective layer on metal surfaces, inhibiting the electrochemical reactions that cause corrosion. Terpenoids can work as corrosion inhibitor agents through several mechanisms, including forming a passive layer on the metal surface, absorbing on the metal surface to protect against corrosive substances, and changing the electrochemical characteristics at the metal-solution interface. Terpenoids have additional advantages as corrosion inhibitor agents because they are more natural and environmentally friendly than many corrosive chemical compounds or synthetic corrosion inhibitors [16-20].
Experimental studies on terpenoids as corrosion inhibitors have yet to be widely published. On the other hand, molecular modeling can provide an initial insight into the potential of green organic compounds as corrosion inhibitors [21-25]. Lemonal terpenoids as copper corrosion inhibitors using DFT have been previously studied. The theoretical studies can

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also differentiate the corrosion inhibition performance of the two lemonal isomers [26]. Theoretical studies can be a bridge in explaining phenomena that are difficult to explain by experimental studies. Simulations can be carried out under conditions very similar to experiments using an accurate method for the model to be studied so that the results of computational chemistry calculations can be compared directly with experimental results. In addition, by using computational chemistry, it is possible to calculate the properties of complex molecules with calculation results that correlate significantly with experiments; with computational chemistry, the costs and time for research can be reduced [27-30]. This research focuses on studying the monoterpenoid compounds thymol, carvacrol, and thymohydroquinone as copper corrosion inhibitors using DFT and MP2 approaches as well as Monte Carlo Simulation.

2 Research Methods

The electronic properties of thymol, carvacrol, and thymohydroquinone in inhibiting corrosion on copper surfaces were studied using Gaussian 09 [31]. The DFT theory level and MP2 ab initio 6-311++G (d,p) were applied to calculate the electronic parameters. Koopmans' theorem [32] is used to measure EHOMO and ELUMO, using equation (1) (2):

$$I = -\ EHOMO \tag{1}$$

$$A = -\ ELUMO \tag{2}$$

Electronegativity (χ), according to Pauling, is a measure of how strongly an atom attracts electrons in a chemical bond when interacting with other atoms. It is an important concept in chemistry because it affects the nature of chemical bonds and the polarity of molecules [33]. Electronegativity values can be calculated using equation (3):

$$\chi = \frac{I+A}{2} \tag{3}$$

Hardness (η) measures atomic resistance to charge transfer [33]. The hardness value can be calculated using equation [33]:

$$\eta = \frac{I-A}{2} \tag{4}$$

The number of electrons transferred [34.35] can be calculated using equation (5):

$$\Delta\chi = \frac{\chi Cu - \chi Inh}{2(\eta Cu + \eta Inh)} \tag{5}$$

Where χCu and χinh denote the absolute electronegativity of copper and organic inhibitors, respectively, ηFeCu and ηinh indicate the absolute hardness of copper and organic inhibitors, respectively. In this study, the theoretical values of χCu = 7.0 eV and ηCu = 0 are used to calculate the number of electrons transferred [36,37].

Monte Carlo simulation was carried out to imitate the real corrosion environment. Monte Carlo simulation was used to search for the lowest adsorption energy configuration of the interaction of the bioactive molecules thymol, carvacrol, and thymohydroquinone on the surface of copper (Cu) and 100 water molecules. Monte Carlo simulations were carried out using Material Studio 7.0 [38,39]. The copper surface can be represented by a Cu(111) plane. Cu(111) planes were used because they are the most stable and have moderate atomic density [40]. The solvent effect of water was simulated by loading 100 geometrically optimized water molecules using the KOMPASS force field into the simulation box along with each organic inhibitor and Cu(111) surface used [41].

3 Results and Discussions

One factor that influences an inhibitor's corrosion inhibition ability is its molecular structure and electronic properties. A quantum chemical approach was used to study this in more detail. Figure 1 shows the structures of studied thymol, carvacrol, and thymohydroquinone.

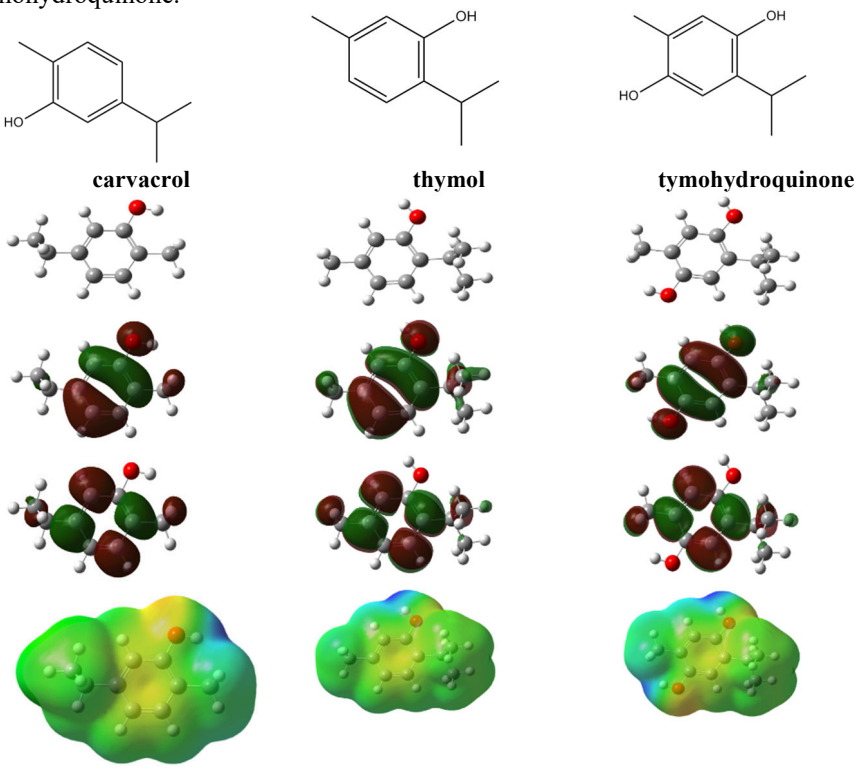

Figure 1. Structure, HOMO-LUMO, and MAPS visualization of the monoterpenoid thymol, carvacrol, and thymohydroquinone

Table 1. Quantum parameters of the thymol, carvacrol, and thymohydroquinone

	carvacrol		**thymol**		**tymohydroquinone**	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
HOMO	-6.0011	-8.2828	-5.9788	-8.2080	-5.4648	-7.8246
LUMO	-0.1578	3.6392	-0.1945	3.5948	-0.1722	3.5415
ΔEgab	-5.8433	-11.9220	-5.7843	-11.8029	-5.2926	-11.3661
I	6.0011	8.2828	5.9788	8.2080	5.4648	7.8246
A	0.1578	-3.6392	0.1945	-3.5948	0.1722	-3.5415
χ	3.0795	2.3218	3.0867	2.3065	2.8185	2.1415
η	2.9216	5.9610	2.8921	5.9014	2.6463	5.6830
ΔN	0.2396	0.1810	-3.0867	0.1841	0.3139	0.2057

EHOMO is related to the capacity of molecules to provide metals with electron donations. High EHOMO values show compounds' propensity to give electrons to acceptor molecules [42]. Therefore, the strength of the organic inhibitory molecules' attachment to the metal

surface is inversely proportional to the EHOMO value. Based on the EHOMO value, predicting organic inhibitors with the highest corrosion inhibition effectiveness values is possible. The quantum properties of the bioactive compounds thymol, carvacrol, and thymohydroquinone determined using the DFT/6-311++G and MP2/6-311++G methods are shown in Table 1. Table 1 shows that thymohydroquinone had the highest EHOMO values and the highest correlation with the copper metal's corrosion inhibition efficiency. It can be seen that thymohydroquinone EHOMO is -7.8246 eV. The ability of thymohydroquinone to donate electrons to copper metal is improved by inserting a double hydroxyl group into the cyclic ring. Figure 1 depicts how the three compounds' HOMO orbitals' electron distributions are distributed.

EHOMO and ionization potential have a direct relationship [42]. Equation 1 can be used to compute the ionization potential value. According to Table 1, thymohydroquinone has a lower ionization potential than thymol (8.2080 eV) and carvacrol (8.2828 eV). Based on this ionization potential, it is possible to forecast that thymohydroquinone has a greater inhibitory efficiency value than thymol and carvacrol. The ionization potential value is the least amount of energy needed for electrons to be released from their bonds and bind to the surface of a metal, shielding it from corrosive environments. Therefore, the inhibitory efficiency value can be increased by a low ionization potential value [43].

The theory of chemical reactivity has been found to be most strongly influenced by electronegativity (χ). For the chemical potential to be balanced when organic inhibitors and copper metal interact, electrons will flow from a lower electronegativity value (organic inhibitor) to a high electronegativity value (Cu) [43]. Equation 3 is used to compute the electronegativity values. The results of computations utilizing the MP2/6-311++G (d,p) approach are shown in Table 1. Thymohydroquinone has the lowest electronegativity value, 2.1415 eV. The other molecules, thymol and carvacrol, had electronegativity values of 3.0867 eV and 3.0795 eV, respectively. The electronegativity value predicts that, when compared to the other three inhibitors, thymohydroquinone has the highest corrosion inhibition efficiency value.

Equation 5 calculates the number of electrons transported (ΔN) from the inhibitor to the metal. According to the value of electron transfer, the value of inhibitory efficiency is produced by the electron donor [44]. As the ability to contribute electrons to the Cu metal surface increases, more electrons will coat the Cu surface. Inhibited corrosion processes can result in electron transfer values [38]. Thymohydroquinone, carvacrol, and thymol are listed in order of their ability to transfer electrons from high to low. The size of this electron donor can explain Thymohydroquinone's greater contribution to corrosion inhibition effectiveness.

MEP explains reactivity and the connection between a molecule's structure and activity. The structure of a molecule is shown by the shape, size, charge density distribution, and location of chemical reactivity in the electron density surface plot mapped with MEP. The MEP surface's color scheme is red, which denotes abundant electrons and a partial negative charge; blue, which denotes a lack of electrons and a partial positive charge; light blue, which denotes a region that is slightly electron deficient; yellow, which denotes a region that is slightly electron rich; and green, which denotes neutrality [44]. Figure 1 displays the MEP plot of the organic inhibitors thymol, carvacrol, and thymohydroquinone. In blue, the electron density is low. In the thymohydroquinone structure, the brownish oxygen atoms (red to green) have a higher electron density. It could mean that the oxygen atom in the thymohydroquinone structure has a high electron density, attracting the Cu surface as a region of low electron density. As opposed to MEP, the Fukui function is a more precise indicator of the portion of the organic inhibitor exposed to electrophilic or nucleophilic assault. The MEP merely defines the alteration in an atom's electron density brought on by adding or subtracting charges.

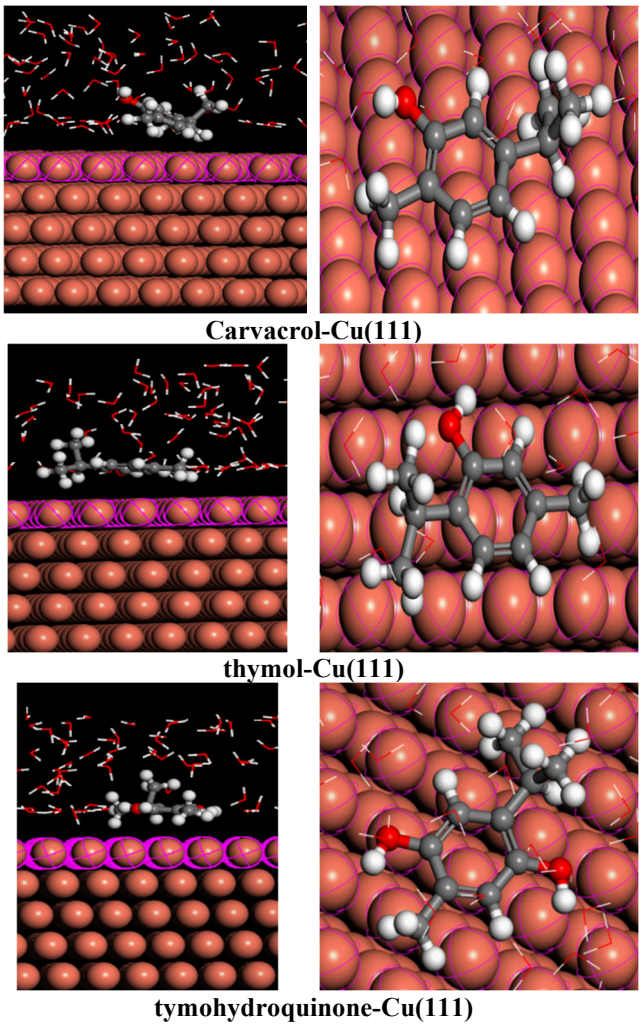

Fig. 2. Monte Carlo Simulation system of adsorption of thymol, carvacrol, and thymohydroquinone in copper surface

Monte Carlo simulations were performed on organic inhibitor systems, water molecules, and metal surfaces. The adsorption characteristics of the inhibitor and 100 water molecules on the Cu(111) metal surface were investigated using Monte Carlo simulations [45]. Because it possesses the most stable surface, the Cu(111) surface is utilized in the Monte Carlo simulation procedure. Figure 2 demonstrates that the Cu(111) surface, which has 100 water molecules and organic inhibitors (thymol, carvacrol, and thymohydroquinone), has the most stable adsorption pattern. The expected organic inhibitor is adsorbed on the surface of Cu(111) as a result of equilibrium occurring in this system. Thymol, carvacrol, and thymohydroquinone are organic inhibitors that can give electrons to the Cu(111) surface because they each include an oxygen atom and a methane cyclic ring. It occurs as a result of vacant orbitals on the Cu(111) surface having the ability to speed up the adsorption process by allowing organic inhibitors to receive electrons and establish stable coordinate bonds. According to Table 2, the systems Cu(111)/thymohydroquinone/100H_2O, Cu(111)/thymol/100H_2O, Cu(111)/carvacrol/100H_2O, and Cu(111)/thymol/100H_2O had the highest adsorption energies for the most stable configurations.

Table 2. Adsorption energy of Cu(111)/monoterpenoid/100H_2O system with Monte Carlo simulation

Compound	Metals	Inhibitors (dEad/dNi)	Water (dEad/dNi)
carvacrol	Copper	-63.90	-16.73
thymol	Copper	-67.84	-15.62
tymohydroquinone	Copper	-79.43	-16.83

In comparison to 100 water molecules, monoterpenoid molecules have a greater adsorption energy. Figure 2 displays the organic inhibitor's and water's adsorption energy distributions. It is possible to distinguish between the distributions of adsorption energies for each organic inhibitor and water. This is because monoterpenoid molecules can create a thick coating, making them ideal for preventing corrosion on the surface of copper metal. Thymohydroquinone dominates the adsorption energy of organic inhibitors on the Cu(111) surface in the presence of 100 water molecules. It is foreseeable that thymohydroquinone will block more effectively than thymol and carvacrol.

4 Conclusion

Thymol, carvacrol, and thymohydroquinone are monoterpenoids that can reduce corrosion. It was explained from the electronic side of the inhibitor molecule using quantum chemistry calculations and Monte Carlo simulations. Quantum chemical parameters are calculated using ab initio MP2 techniques and density functional theory. Thymohydroquinone has the strongest corrosion inhibition potential, which is explained by quantum characteristics. The adsorption energy demonstrates how effective thymohydroquinone is at preventing corrosion on copper metal.

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