RESEARCH ARTICLE | MARCH 18 2024

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AIP Conf. Proc. 3026, 030006 (2024)
https://doi.org/10.1063/5.0199768

Copper corrosion inhibition by some monoterpenoids: A theoretical study

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Abstract. Density functional theory (DFT), *ab initio*, and Monte Carlo simulations have been used to study the corrosion inhibition of copper by the monoterpenoids menthol, isopulegol, terpinen-4-ol, and α-terpineol. Quantum chemical parameters to provide information about the electronic properties of the tested molecule as a corrosion inhibitor. Monte Carlo simulations present target molecules' dynamics and inhibition mechanisms on copper surfaces. Quantum parameters and adsorption energy results show that α-terpeneol has the potential to have the highest corrosion inhibition efficiency.

INTRODUCTION

Copper corrosion is a problem in industrial processes. The use of inhibitors is one method of preventing metal corrosion [1-4]. The currently available inhibitors are inorganic. These inhibitors have environmental problems, high heavy metal concentrations, and are toxic. Natural product-based organic inhibitors are substitutes for inhibitors [5-9]. Many studies of corrosion inhibition by organic inhibitors have been carried out, such as the heterocyclic group [10,11], the aromatic group [12,13], etc.

Essential oils produced from natural organic materials have been widely reported as potential inhibitors of corrosion. Apart from having no side effects, inhibitors from essential oils can be easily obtained, the price is low, and they have high biodegradability [14-19]. These inhibitors form a thin layer on the metal surface to prevent corrosion from occurring. Of the various types of organic inhibitors, essential oils from monoterpenoid essential oils can inhibit corrosion. The menthol, isopulegol, terpinen-4-ol, and α-terpineol compounds have hydroxyl groups at different positions on the cyclic ring, with double bonds that allow interaction with the metal surface. For example, the literature indicates that menthol is a suitable corrosion inhibitor.

Experimentally the efficiency of corrosion inhibition can be calculated accurately [20,21]. However, the electronic properties of inhibitors and metals when the inhibition process occurs have yet to be studied in more detail. A more detailed study of the interaction pattern of essential oils and the mechanism of corrosion inhibition is still needed. The theoretical approach is alternated solutions to bridge the problem. Theoretical studies have been widely used to explain the corrosion inhibition mechanism [22-30]. The DFT-TB study was conducted to examine the monoterpenoids carvacrol and thymol. The simulation was carried out on the inhibitor on the Copper surface. Theoretical studies have proven to effectively overcome the difficulties encountered in experimental studies. Quantum chemical methods have proved very useful in determining the structure of molecules and can explain reactivity and electronic structure. The current study focuses on applying DFT, *ab initio* MP2, and Monte Carlo simulation to study the electronic properties and interaction patterns between the monoterpenoids menthol, isopulegol, terpinen-4-ol, and α-terpineol.

The 7th International Conference on Science and Technology (ICST22)
AIP Conf. Proc. 3026, 030006-1–030006-6; https://doi.org/10.1063/5.0199768
Published by AIP Publishing. 978-0-7354-4894-0/$30.00

METHODS

DFT and *ab initio* approach

For the study of corrosion inhibition of natural products based on quantum parameters, quantum chemical computations are frequently performed. The structure, electron distribution, and electron transfer of the monoterpenoids menthol, isopulegol, terpinen-4-ol, and -terpineol to the copper (Cu) surface are predicted using quantum chemical simulations. DFT and *ab initio* MP2 at 6-311++G (d,p) level of theory are used in quantum chemical computations and are implemented in the Gaussian software 09 W [31]. Quantum chemical characteristics can describe the reactivity of a molecule as EHOMO, ELUMO, EGAP (E), ionization potential (I), electron affinity (A), electronegativity (E), hardness (H), and electron transfer (ΔN). Using equations (1) and (2), According to Koopmans' Theorem [32], ionization potential (I) and electron affinity (A) are related to the values of EHOMO and ELUMO, respectively, respectively:

$$I = - EHOMO \quad (1)$$

$$A = - ELUMO \quad (2)$$

Equation (3) can be used to obtain electronegativity (χ) values [33].

$$\chi = \frac{I+A}{2} \quad (3)$$

Equation (4) [33] can be used to calculate the hardness (η) value.

$$\eta = \frac{I-A}{2} \quad (4)$$

The number of electrons transferred ΔN [34,35] can be calculated using equation (5):

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

where χCu and χinh stand for the relative absolute electronegativities of organic inhibitors and copper. The symbols ηCu and ηinh, which stand for the absolute hardness of copper and organic inhibitors, respectively. The ΔN is determined using the theoretical values of Cu = 4.43 eV and Cu = 0 [36,37].

Monte Carlo Simulation

The Monte Carlo simulation was carried out using Material Studio 7.0 [38,39]. In order to identify the configuration with the lowest adsorption energy, the interaction of the monoterpenoid substances menthol, isopulegol, terpinen-4-ol, and -terpineol with the surface of copper (Cu) and 100 water molecules was investigated. The copper surface can be imitated using the Cu (111) plane. The Cu (111) field is used because it is the most stable and has a low atomic density [40]. The water-dissolving impact was simulated by loading 100 geometrically optimized water molecules along with each organic inhibitor and Cu (111) surface into the simulation box [41]. The goal of this Monte Carlo simulation is to simulate the corrosion environment in the actual world.

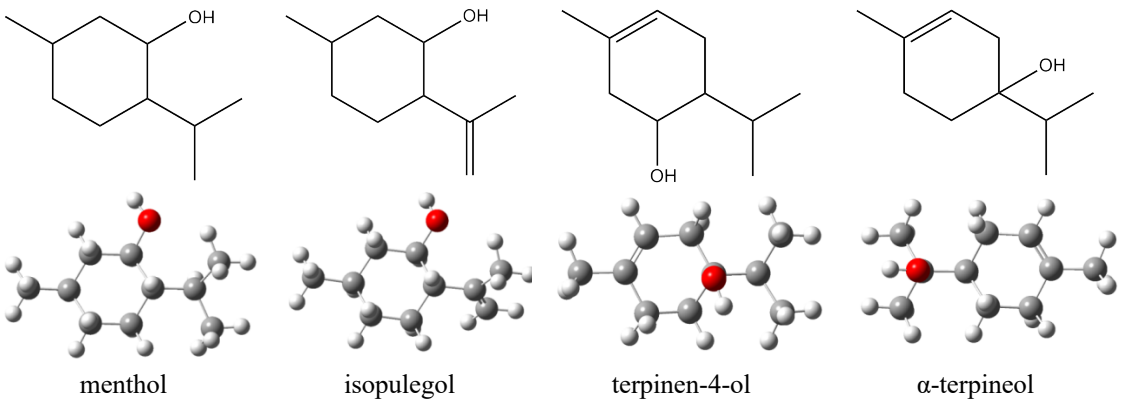

FIGURE 1. Structure of the monoterpenoid menthol, isopulegol, terpinen-4-ol, and α-terpineol

TABLE 1. Quantum parameters of the monoterpenoid menthol, isopulegol, terpinen-4-ol, and α-terpineol

Inhibitors	Method	EHOMO (eV)	ELUMO (eV)	I (eV)	A	χ	η	ΔN
menthol	B3LYP	-7.2741	0.9156	7.2741	-0.9156	3.1792	4.0948	0.158
	MP2	-11.1596	4.0906	11.159	-4.0906	3.5344	7.6251	0.062
isopulegol	B3LYP	-6.5538	0.5385	6.5538	-0.5385	3.0076	3.5461	0.207
	MP2	-9.1231	4.0939	9.1231	-4.0939	2.5145	6.6085	0.148
terpinen-4-ol	B3LYP	-6.2877	0.5932	6.2877	-0.5932	2.8472	3.4404	0.237
	MP2	-8.8455	3.9154	8.8455	-3.9154	2.4650	6.3805	0.157
α-terpineol	B3LYP	-6.2069	0.6163	6.2069	-0.6163	2.7952	3.4116	0.246
	MP2	-8.7794	3.8925	8.7794	-3.8925	2.4434	6.3360	0.160

EHOMO exhibits the capacity to provide metals with electrons from other compounds. An increased chance for molecules to donate electrons to acceptors is indicated by a high EHOMO value [42]. Therefore, the more the organic inhibitory molecules bond to the metal surface, the greater the EHOMO value. The monoterpenoid compounds menthol, isopulegol, terpinen-4-ol, and α-terpineol's quantum parameters are displayed in Table 1. Table 1 shows α -terpineol has the greatest EHOMO value, followed by terpinen-4-ol, isopulegol, and menthol. As shown, α-terpineol has a lower EHOMO than menthol, isopulegol, and terpinen-4-ol at -8.7794 eV. The ability of α-terpineol to donate electrons to copper metal is improved by adding a double bond to the cyclic ring. Figure 2 shows the distribution of the four compounds' HOMO orbitals' electron distribution.

The smallest amount of energy needed to zap an electron is known as the ionization potential. Inhibitors are better able to bind to metal surfaces and stop corrosion due to the release of electrons. The value of corrosion inhibition efficiency rises when the ionization potential is low [43]. Equation 1 is a formula that can be used to compute the potential ionization value [42]. In comparison to terpinen-4-ol (8.84558 eV), isopulegol (9.12314 eV), and menthol (whose lowest potential ionization value is shown in Table 1 as 8.7794 eV), α -terpineol has the lowest ionization potential value. Compared to menthol, isopulegol, and terpinen-4-ol, terpinen-4-ol has a better value for corrosion inhibition efficiency.

From materials with lower electronegativity (organic inhibitors) to those with high electronegativity (Cu), electrons will move [43]. The lowest electronegativity for α -terpineol is 2.4434 eV, as seen in Table 3. Terpinen-4-ol, isopulegol, and menthol were the other molecules, and their electronegativity values were 2.4650 eV, 2.5145 eV, and 3.5344 eV, respectively. Comparing the three inhibitors, α-terpineol is projected to have the highest corrosion inhibition efficiency.

The electron transfer value ΔN can indicate the effectiveness of corrosion inhibition [44]. Equation 5 is utilized to determine ΔN. The coating of the inhibitor on the Cu surface increases with the number of electrons on the Cu metal surface [44]. The ability to transmit electrons is ranked from high to low as follows: α-terpineol > terpinen-4-ol > isopulegol > menthol. It clarifies why α terpineol increases the effectiveness of corrosion inhibition. The monoterpenoids menthol, isopulegol, terpinen-4-ol, and α-terpineol's MEP plot can be shown in Figure 2. Blue has a low electron density. The reddish-brown color of the oxygen atoms in the cyclic double bond indicates a higher electron density. Due to the high electron density, the inhibitor adheres to the Cu surface quite quickly.

The monoterpenoids, water molecules, and copper surfaces are all included in the Monte Carlo simulation. Monte Carlo simulations can be used to thoroughly examine the adsorption of monoterpenoids and 100 water molecules on the surface of Cu (111) metal [45]. The most stable adsorption pattern, represented by the 100 water molecules and monoterpenoids (menthol, isopulegol, terpinen-4-ol, and α-terpineol) present on the Cu (111) surface in Figure 3, is shown. To provide electrons to the Cu (111) surface, each monoterpenoid has an oxygen atom and a double bond in the ring. By receiving electrons from monoterpenoids, the empty orbitals on the Cu (111) surface can aid in the adsorption process [46]. The adsorption energies for the most stable configurations of Cu (111)/terpinen-4-ol/100H2O, Cu (111)/isopulegol/100H2O, and Cu(111) systems/menthol/100H2O are shown in Table 2. Monoterpenoids can securely bind to the copper surface because their adsorption energy is higher than water molecules.

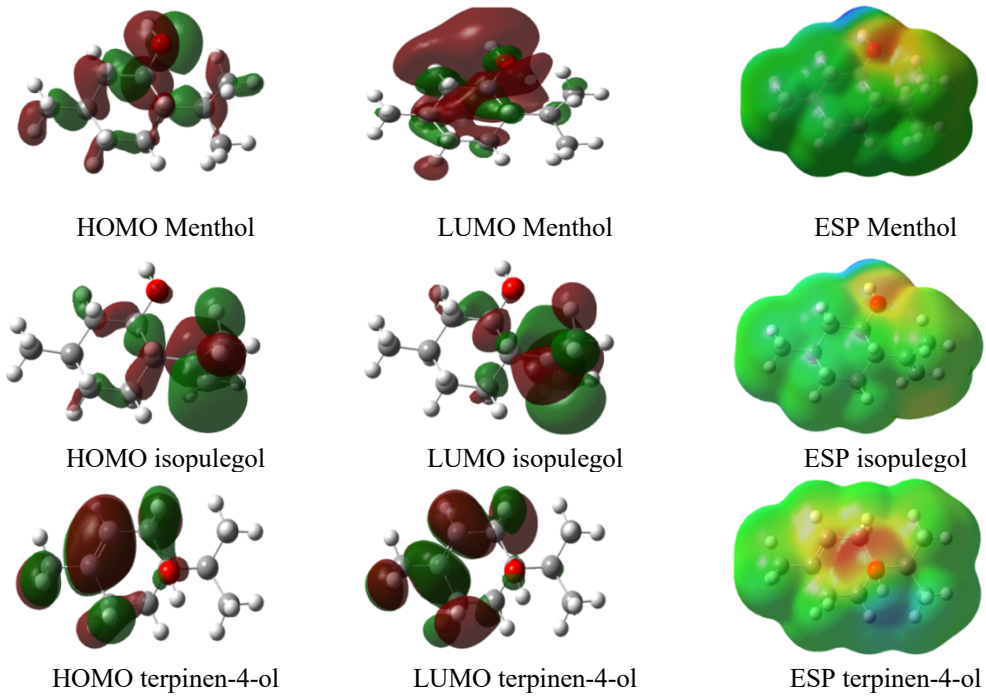

FIGURE 2. HOMO-LUMO and ESP visualization of menthol, isopulegol, terpinen-4-ol, and α-terpineol

TABLE 2. Adsorption energy of Cu(111)/monoterpenoid/100H2O system with Monte Carlo simulation

Compounds	Metals	Inhibitors (dEad/dNi)	Water (dEad/dNi)
menthol	Copper	-57.55268891	-15.61076704
isopulegol	Copper	-64.19563798	-16.12062619
terpinen-4-ol	Copper	-57.62598781	-16.45251016
α-terpineol	Copper	-62.13010523	-15.70503472

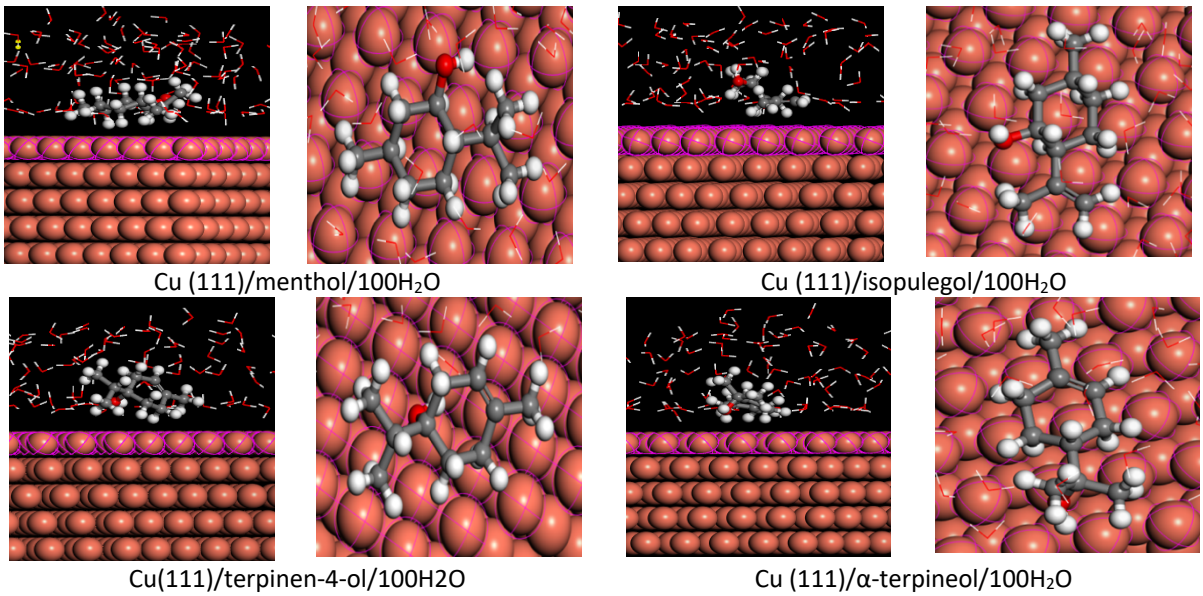

FIGURE 3. Monte Carlo Simulation system of adsorption of menthol, isopulegol, terpinen-4-ol, and α-terpineol in copper surface

CONCLUSION

According to experimental research, monoterpenoid molecules can be corrosion inhibitors. But experimental research still needs to provide detailed explanations of the electron characteristics that lead to corrosion inhibition. It was explained from the electronic side of the inhibitor molecule using quantum chemistry calculations and Monte Carlo simulations. Terpinen-4-ol and a-terpineol can suppress corrosion on copper metal more effectively, according to quantum characteristics and adsorption energy

ACKNOWLEDGMENTS

Gratefully acknowledges financial support from Kemendikbudristek Indonesia.

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