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A DFT STUDY OF N-ACETYLCYSTEINE AND D-PENICILLAMINE AS CORROSION INHIBITORS FOR COPPER

Gökhan Gece[1†], Semra Bilgiç[2]

[1]Department of Chemistry, Bursa Technical University, 16310 Bursa, TÜRKİYE
[2]Department of Chemistry, Ankara University, 06100 Ankara, TÜRKİYE

ABSTRACT. The most popular and accessible corrosion inhibitors, i.e., silicates, chromates, phosphates, nitrites, amines, and numerous formulations based on these compounds, are toxic and fail to produce a universal effect. Amino acids and their derivatives are non-toxic, relatively cheap, biodegradable compounds. These molecules can form a barrier through adsorption on the copper surface to reduce the corrosion, and it has been observed that the adsorption depends mainly on the coordination of bidentate ligands, which occurs through an amino or carboxyl group and thiol group -SH. In recent years, there has been considerable progress in the description of the structure and inhibition properties of corrosion inhibitors by using quantum chemical calculations. In this study, the molecular and electronic structures of N-acetylcysteine and D-penicillamine have been justified by comparing the theoretical data from the density functional theory (DFT) method with experimental corrosion inhibition efficiencies. The theoretical results were found to be consistent with the reported experimental data.

1. INTRODUCTION

Copper, a widely used metal in various industries, is prone to corrosion, particularly in chloride-rich environments. The presence of chloride ions accelerates the corrosion process, leading to significant material degradation and economic losses. To mitigate this issue, researchers have explored various corrosion inhibition strategies, including the use of organic compounds [1].

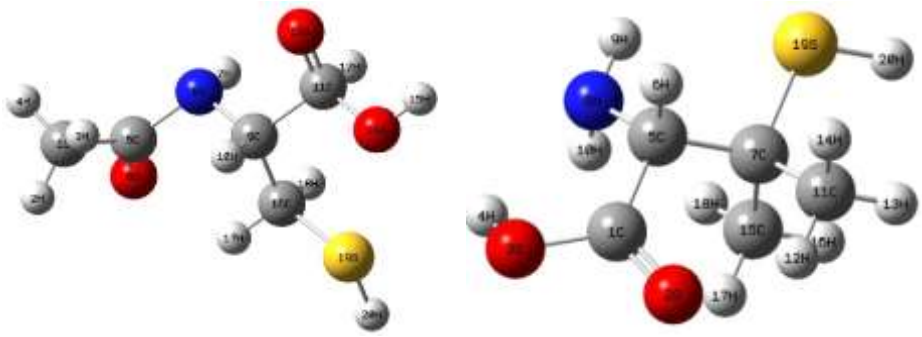
Keywords. Corrosion, inhibition, density functional theory, N-acetylcysteine, D-penicillamine.

[1] gokhangc@gmail.com-Corresponding author; 0000-0001-9310-5407
[2] bilgic@science.ankara.edu.tr; 0000-0001-9730-0146.

In recent years, amino acids have emerged as promising corrosion inhibitors for copper. These biomolecules, with their diverse functional groups, can interact with the metal surface, forming protective films and hindering the corrosion reactions. Several studies have reported the effectiveness of different amino acids in inhibiting copper corrosion in chloride solutions. For example, cysteine, with its sulfur-containing thiol group, has been shown to exhibit excellent inhibition properties by forming strong bonds with the copper surface [2].

To gain deeper insights into the inhibition mechanisms, Density Functional Theory (DFT) calculations have been employed. DFT allows for the investigation of the electronic structure, adsorption energies, and charge transfer between the amino acid molecules and the copper surface [3]. By understanding these interactions at the atomic level, researchers can identify the most effective inhibitors and design novel compounds with improved performance [4].

While the use of amino acids as corrosion inhibitors offers a promising approach, further research is needed to fully understand the underlying mechanisms and optimize their performance. By combining experimental studies with theoretical calculations, researchers can develop more effective and environmentally friendly corrosion inhibitors for copper and other metals. In this regard, the inhibition efficiency of N-acetylcysteine (Fig. 1a) and D-penicillamine (Fig. 1b) as inhibitors of copper corrosion in 3% NaCl solution has been recently studied experimentally by Martinović et al. [5].



a b

Figure 1. Optimized structure of (a) N-acetylcysteine and (b) D-penicillamine.

N-acetylcysteine and D-penicillamine have been used in medicine for decades. N-acetyl cysteine is primarily known for its use in treating acetaminophen overdose, but it also has applications in respiratory conditions like chronic bronchitis. D-penicillamine, on the other hand, has been used to treat Wilson's disease, a rare genetic disorder of copper metabolism, and rheumatoid arthritis [6,7].The aim of the present computational study is to analyze the nature of the interaction of these two compounds with the copper surface in order to verify how the corrosion inhibition process takes place.

2. COMPUTATIONAL DETAILS

The optimal electronic ground state geometries of the studied inhibitors were optimized by the DFT employing Becke's three parameter hybrid functional using the Lee, Yang and Parr correlation functional (B3LYP). The obtained optimal structures were confirmed by the standard normal mode analysis.The Hessian index of zero has been computed, and all of the forces are positive. All the calculations were performed via Gaussian09 [8]. Assuming the validity of Koopmans theorem, the simulation of the vertical ionisation energy in the first stage of the molecules and the vertical electron affinities were carried out using the Kohn-Sham formalism. On the basis of optimized B3LYP geometries, the vertical ionisation energy (I) (Eq. 2.1) and the vertical electron affinity (A) (Eq. 2.2) have been approached in terms of the energies of the boundary molecular orbitals, known as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).The calculation was based on the eigenvalues of the virtual Kohn–Sham orthogonalized orbitals [3].

$$I = -E_{HOMO} \qquad (2.1)$$
$$A = -E_{LUMO} \qquad (2.2)$$

Some electronic descriptors including the dipole moment (Þ) the electronegativity (χ), the chemical potential (μ), the chemical hardness (η), the softness (S), and the electrophilicity index (ω)were calculated according to Eqs. (2.3–2.6) as reported in the literature [3,4,9]:

$$\chi = \frac{(I+A)}{2} \qquad (2.3)$$

$$\eta = \frac{(I-A)}{2} \qquad (2.4)$$

$$S=\frac{1}{2\eta} \qquad (2.5)$$

$$\omega = \frac{\mu^2}{2\eta} \qquad (2.6)$$

Solvent contributions of water (H_2O) were computed employing the solvation model with solute electron density (SMD) [10].

3. RESULTS AND DISCUSSION

N-acetylcysteine is most abundant in plants of the genus Allium, especially onions, and is a precursor of the amino acid L-cysteine [6]. On the other hand, D-penicillamine, is a sulfur-containing amino acid drug used to treat several diseases [7,11]. As reported by Martinović et al. [5], higher inhibition efficiency (IE) values found for N-acetylcysteine compared to those D-penicillamine could be explained in terms of the adsorption capability as bidentate ligands with coordination occurring through an amino or carboxyl group and thiol group -SH. The intrinsic characteristics of these compounds in their uncharged states can be examined in detail. Molecular orbital analysis, a prevalent technique for scrutinizing chemical interactions, provides valuable insights into their electronic configurations.

The fundamental nature of HOMO-LUMO interactions has been elucidated in relation to the transformation of molecular geometry along the reaction pathway. While this concept is inherently complex, E_{HOMO} serves as a reliable indicator of a molecule's electron-donating capacity. Higher E_{HOMO} values are thus regarded as markers of superior electron donation, leading to enhanced adsorption of the inhibitor onto mild steel and consequently, improved inhibition efficiency. Conversely, the opposite trend holds true for E_{LUMO}. As this parameter reflects the electron-accepting tendency, lower E_{LUMO} values are considered optimal for achieving the highest efficiency. The energy gap of the molecule ($\Delta E_{L\text{-}H} = E_{LUMO} - E_{HOMO}$) is determined by the difference between E_{LUMO} and E_{HOMO}, enabling the skillful application of molecular softness or hardness concepts. Soft molecules exhibit greater reactivity compared to hard molecules [3].

A comparative analysis of the electronic properties in the context of these explanations would be beneficial. Table 1 presents a correlation

between certain quantum chemical parameters associated with these molecular electronic structures and the corresponding experimental inhibitory efficacy percentages.

Table 1. Molecular electronic parameters of two inhibitors calculated at the B3LYP/6-311G(d,p) level of theory.

Parameters	Phase [b]	N-acetyl cysteine	D-penicillamine
avg. IE (%)[a]		69.9	67.2
E_{HOMO} (eV)	G	-4.940	-6.903
	A	-4.607	-6.613
E_{LUMO} (eV)	G	-0.415	-0.369
	A	-0.237	-0.183
ΔE (eV)	G	4.525	6.534
	A	4.370	6.430
ω	G	1.585	2.023
	A	1.342	1.796
χ	G	2.678	3.636
	A	2.422	3.398
η	G	2.263	3.267
	A	2.185	3.215
S	G	0.221	0.153
	A	0.229	0.156
Þ (D)	G	2.129	3.407
	A	4.957	4.944
ΔN	G	-0.436	-0.155
	A	-0.509	-0.195

[a]Ref. [5]. [b]G: gas phase (ε = 1.0); A: aqueous phase (ε = 78.5)

The frontier molecular orbital pictures of the both molecules are shown in Figure 2. As can be seen, the HOMO of D-penicillamine is mainly localized in the non-ligand π orbital of thiol group, while its LUMO has an anti-ligand π character involving the acid and amine groups. On the other hand, the reactive site for electrophilic attack located on the sulfur atom of N-acetyl cysteine can be proved by the distribution of HOMO. From Figure 2, it can also be seen that the LUMO is located not only in the carboxylic acid groups but also in the benzene ring.

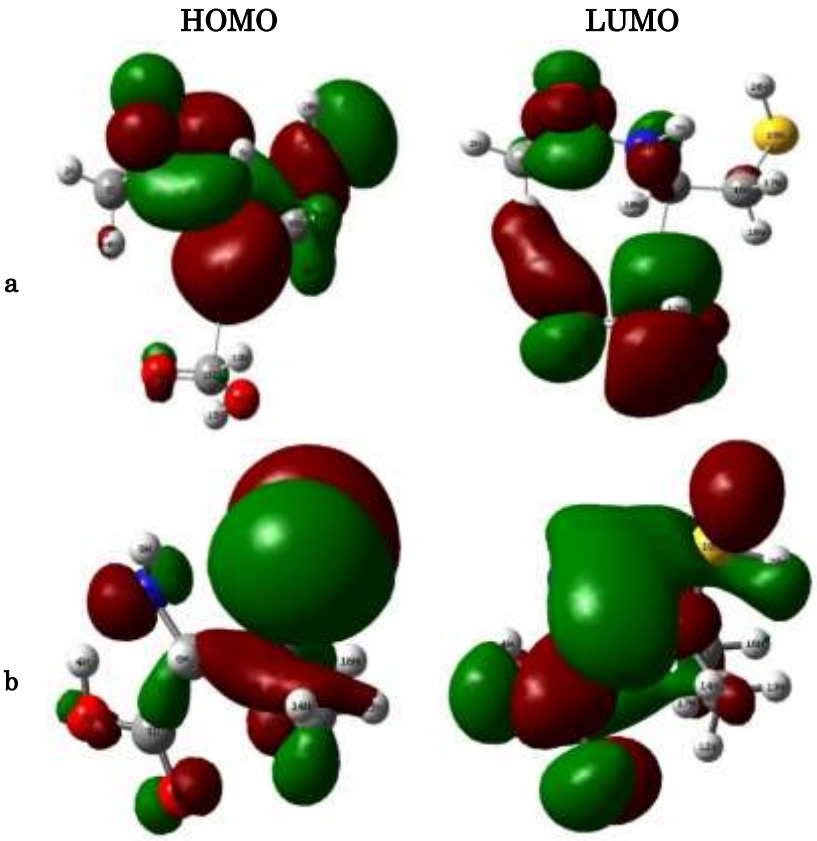


Figure 2. Comparisons of HOMO and LUMO contours for (a) N-acetyl cysteine and (b) D-penicillamine.

The tabulated data in Table 1 clearly reveals that N-acetyl cysteine exhibits higher HOMO energies and lower LUMO energies compared to

D-penicillamine in both phases. As a result, N-acetyl cysteine possesses smaller energy gap values than D-penicillamine. Consequently, electron transfer from the HOMO to LUMO is facilitated in N-acetyl cysteine relative to D-penicillamine. A lower ω value signifies a more reactive nucleophile, whereas a higher ω value characterizes a potent electrophile. In this context, N-acetyl cysteine appears to function as a nucleophile in both phases. Molecules with a large energy disparity are classified as hard, while those with a small energy disparity are considered soft. Soft molecules, due to their ease of electron donation to acceptors, exhibit higher reactivity than hard molecules. As observed, N-acetyl cysteine displays lower η and higher S values than D-penicillamine in both phases. Dipole moment serves as a measure of the polarity of a polar covalent bond. It is defined as the product of the charge on the atoms and the inter-atomic distance. While its correlation with inhibition efficiency remains debatable, dipole moment is still considered a significant parameter. In this study, the theoretical findings indicate an absence of a direct relationship between Þ and inhibition efficiency.

The number of transferred electron, ΔN, was also given by the equation as following:

$$\Delta N = \frac{\chi_{Cu} - \chi_{inh}}{2(\eta_{Cu} + \eta_{inh})} = \frac{\Phi - \chi_{inh}}{2\eta_{inh}} \qquad (3.1)$$

Here, Φ is the work function that corresponds to the copper's theoretical electronegativity value (Φ = χ_{Cu} = 4.65 eV), and the global hardness accounts for the copper heft (η_{Cu} = 0 eV). In general, the fraction of transferred electrons is also smaller for N-acetyl cysteine. If ΔN< 3.6, the inhibition efficiency increases by increasing electron donating ability to the metal surface. Therefore, the inhibitive effectiveness order is: N-acetyl cysteine>D-penicillamine. As a result, a satisfactory agreement has been found between the calculated and experimental data [12].

4. CONCLUSION

The DFT B3LYP/6-311G(d,p) study presented herein successfully corroborates the experimental findings, providing valuable insights into the underlying mechanisms governing corrosion inhibition properties of N-acetyl cysteine and D-penicillamine. The calculated quantum chemical parameters are in well agreement with the experimental observations, validating the reliability of the employed computational approach. These results highlight the power of computational chemistry in elucidating corrosion inhibition processes and offer a robust foundation for future theoretical investigations.

Author Contribution Statement Gökhan Gece—Performing the calculations, analyzing, interpreting, writing, and editing the manuscript. Semra Bilgiç—Planning and reviewing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

REFERENCES

[1] Gece, G., Sustainable Corrosion Inhibitors II: Synthesis, Design, and Practical Applications, ACS Symposium Series, American Chemical Society, Washington, DC, 2021. https://doi.org/10.1021/bk-2021-1404.ch007.

[2] El Ibrahimi, B., Jmiai, A., Bazzi, L., El Issami, S., Amino acids and their derivatives as corrosion inhibitors for metals and alloys, *Arabian Journal of Chemistry* 13 (2020), 740-771. https://doi.org/10.1016/j.arabjc.2017.07.013.

[3] Gece, G., The use of quantum chemical methods in corrosion inhibitor studies, *Corrosion Science* 50 (2008), 2981-2992. https://doi.org/10.1016/j.corsci.2008.08.043.

[4] Gece G., Bilgiç, S., Anti-corrosion characteristics of ampicillin and flucloxacillin drugs: a theoretical study, *Communications Faculty of Sciences University of Ankara Series B Chemistry and Chemical Engineering* 65 (2023), 29–35.

[5] Martinović, I., Pilić, Z., Zlatić, G., Soldo, V., Šego, M., N-acetyl cysteine

and D-penicillamine as green corrosion inhibitors for copper in 3% NaCl, *International Journal of Electrochemical Science* 18 (2023), 100238.https://doi.org/10.1016/j.ijoes.2023.100238.

[6] Mokhtari,V., Afsharian, P., Shahhoseini,M.,Kalantar,S.M.,Moini, A., A review on various uses of N-acetyl cysteine, *Cell Journal* 19 (2017), 11-17. https://doi.org/10.22074/cellj.2016.4872.

[7] Antos, A., Członkowska, A.,Bembenek, J.,Kurkowska-Jastrzębska,I., Litwin, T., D-penicillamine-induced myasthenia gravis - a probable complication of Wilson's disease treatment – a case report and systematic review of the literature, *Life* 13 (2023), 1715. https://doi.org/10.3390/life13081715.

[8] Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M.; Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J. A. Jr., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, Ö., Foresman, J. B., Ortiz, J. V., Cioslowski, J., Fox, D. J., *Gaussian 09, Revision C.01.*, Wallingford CT, Gaussian, Inc., 2009.

[9] Gece, G., Inhibition of steel corrosion by some Schiff and Mannich bases: a theoretical evaluation, *Voprosy Khimii i Khimicheskoi Tekhnologii* 4 (2021), 27-34. https://doi.org/10.32434/0321-4095-2021-137-4-27-34.

[10] Marenich, V., Cramer, C. J., Truhlar, D.G., Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions, *The Journal of Physical Chemistry B* 113 (2009), 6378–6396. https://doi.org/10.1021/jp810292n.

[11] Howard-Lock, H.E., Lock, C.J.L., Mewa, A., Kean, W.F., D-penicillamine: Chemistry and clinical use in rheumatic disease, *Seminars in Arthritis and Rheumatism* 15 (1986), 261-281. https://doi.org/10.1016/0049-0172(86)90022-3.

[12] Lukovits, I., Kalman, E., Zucchi, F., Corrosion inhibitors – correlation between electronic structure and efficiency, *Corrosion* 57 (2001), 3-8. https://doi.org/10.5006/1.3290328.