Creatine and creatinine as copper corrosion inhibitors: A DFT study

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Abstract

The present study aimed to examine the influence of molecular and electronic structure on the corrosion inhibition effects of creatine and creatinine compounds. To this end, density functional theory calculations were conducted to determine various quantum chemical parameters, including the highest occupied molecular orbital energy (E_{HOMO}), lowest unoccupied molecular orbital energy (E_{LUMO}), and energy gap (ΔE) at the B3LYP/6-311G++(d,p) basis set. Furthermore, the global reactivity parameters are evaluated from the vertical ionization potential and electron affinity. It was postulated that no a priori understanding could be derived regarding the corrosion inhibition properties of the studied compounds through the application of calculated descriptors.

Keywords: Corrosion; Inhibitor; Creatine; Creatinine; DFT

1. Introduction

Practically all metallic materials have been exploited in a motley number of applications, and thus are susceptible to corrosion, especially if aggressive ions are present. Several copper-made constructions like heat exchangers usually expose to such aggressive environments in desalination systems and petroleum pipelines. It has long been noted that the addition of chemicals known as corrosion inhibitors, can minimize the extent of corrosion [1]. Compounds with useful corrosion inhibition properties often derive their utility through a collective arrangement of many functional groups and/or atoms. The aspect of how to find a corrosion inhibitor is important not just in how to render its synthesis economic, but more crucially to control its inhibition properties [2].

In this regard, a wide range of copper corrosion inhibitors have been used for several decades [3]. However, regnant corrosion inhibitors have discomfitures such as toxicity and hazardous effects on health and environment. That is why research is needed in order to find the best inhibitors with the desired effects at the least cost. Creatine (N-Carbamimidoyl-N-methylglycine) which is found in the myoserum of vertebrates, and creatinine (2-Amino-1-methyl-1,5-dihydro-4H-imidazol-4-one) which is an end product of muscle metabolism, are (Figure 1) known to be eco-friendly and cost-effective nitrogenous organic compounds [4].

Recently, Al Bahir [5] inspected the performances of these two compounds for the corrosion of copper in 0.5 M NaOH solution using potentiodynamic polarization, electrochemical impedance spectroscopy, and weight loss methods. It has been reported that the values of % inhibition efficiencies of creatine were slightly higher than those acquired for creatinine. Unlike the experimental methods, quantum chemical methods provide the corrosion analyst with a formidable tool to understand such inhibitor-metal surface electronic

interactions [6]. One of the most important quantum chemical methods is the density functional theory (DFT), which measures the electron density $\rho(r)$ around the corrosion inhibitor as an index for interpreting its chemical characteristics and interaction with the corroding metal surface [7].
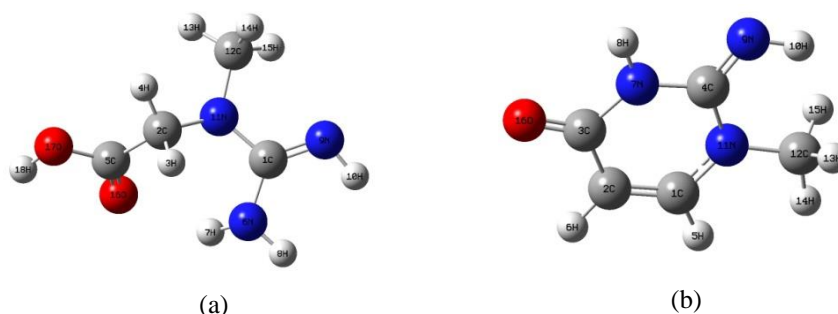

Fig. 1. Optimized structure of (a) creatine and (b) creatinine

This paper is intended to extend Al Bahir's experimental investigation by analyzing the inhibitive properties of creatine and creatinine through the DFT calculations of some quantum chemical parameters. The relevance of existing theoretical frameworks for addressing corrosion inhibition efficiency of such compounds is also discussed.

2. Computational Method

Conceptual density functional theory is a DFT-subfield in which the partial derivatives of electron density and total energy, with respect to the number of electrons and external potentials, allow for the determination of certain global and/or local reactivity descriptors from which the different corrosion inhibition behaviors of compounds can be quantified [8]. Accordingly, the equilibrium geometries and electronic structures of creatine and creatinine are computed using density functional theory and the Gaussian09 package [9]. The exchange–correlation potential is incorporated using the hybrid B3LYP functional, and the basis set considered was 6-311++G(d,p). For calculations in water, a charge-density (D) based solvation model (SM), i.e., the SMD model is used. All the parameters were allowed to relax and calculations converged to an optimized geometry which corresponds to a true minimum, as denoted by the lack of imaginary wave numbers. Some electronic descriptors including the energies of the highest occupied and the lowest unoccupied molecular orbital (E_{HOMO} and E_{LUMO}), the energy gap (ΔE), the electron affinity (EA), the ionization potential (IP), the electronegativity (χ), the chemical hardness (η), the softness (S), and the fraction of electrons transferred (ΔN) were calculated according to Eqs. (1–7) as reported in the literature [10].

$$IP = -E_{HOMO} \qquad (1)$$

$$EA = -E_{LUMO} \qquad (2)$$

$$\Delta E = E_{LUMO} - E_{HUMO} \qquad (3)$$

$$\chi = \frac{(IP+EA)}{2} \qquad (4)$$

$$\eta = \frac{(IP-EA)}{2} \qquad (5)$$

$$S = \frac{1}{\eta} \qquad (6)$$

$$\Delta N = \frac{\phi_{Cu} - \chi_{\text{inhibitor}}}{2(\eta_{Cu} + \eta_{\text{inhibitor}})} \qquad (7)$$

In Eq. 7, the work function Φ presents the theoretical value of electronegativity of copper ($\Phi = \chi_{Cu} = 4.65$ eV), and the global hardness corresponds to the metallic bulk ($\eta_{Cu} = 0$ eV) [11].

3. Results and Discussion

Frontier orbital theory was introduced by Fukui as another measure of reactivity. The frontier electrons are those occupying the filled orbital of highest energy; the idea is that in any interaction with an external agent this orbital should be perturbed more strongly than the rest. The site of the greatest electronic density of the HOMO would presumably correspond to the highest concentration of the most energetic electrons, and these were quite reasonably expected to be the most reactive toward electrophiles. The transfer of electronic charge from the HOMO of a donor molecule to the LUMO of an acceptor molecule is postulated in this theory [12]. HOMO and LUMO distributions of the studied inhibitors are depicted in Figure 2.
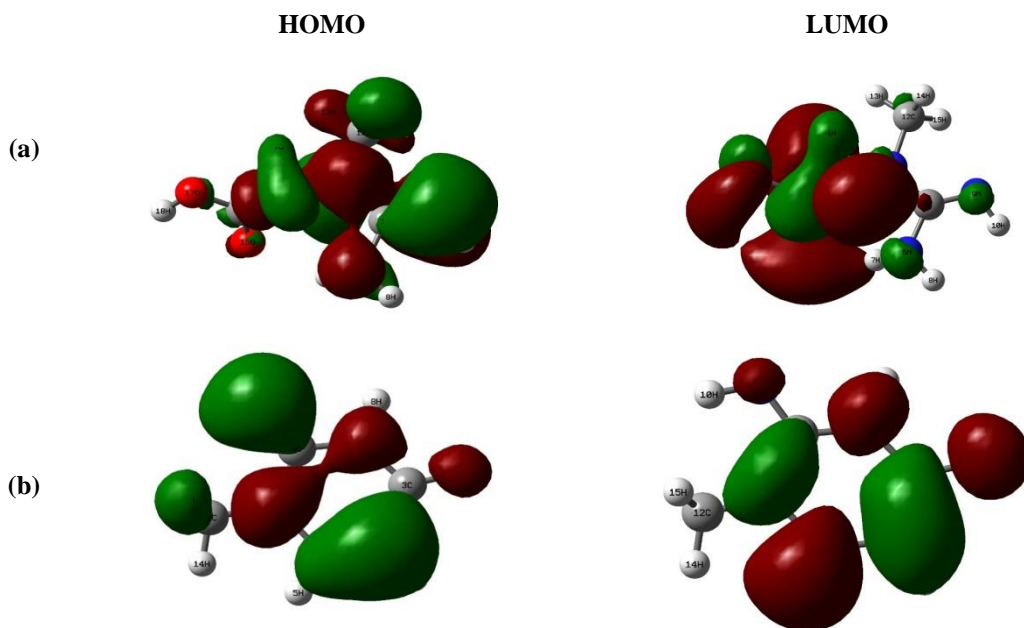
HOMO   **LUMO**

Fig. 2. Molecular orbital surfaces for HOMO and LUMO of (a) Creatine and (b) Creatinine

From Fig. 2, it is observed from the distribution of the electron density HOMO that the electron donating adsorption centers for both systems are localized over the methyl and amidino groups attached to the nitrogen. However, the electron density of LUMO also extends over the same regions as that of HOMO; but in this case, the imidazolidinone ring system is also involved. The inhibition efficiency disparities of the studied molecules are generally explained on the basis which foreholds that high HOMO, low LUMO and small energy gap are associated with better inhibiting properties [13]. In the light of these explanations, it would be appropriate to have a comparison of the electronic features. In Table 1, certain quantum chemical parameters related to these molecular electronic structures have been compared with corresponding percentage values of experimental inhibition efficiencies (IE). The theoretical data in Table 1 show that in both gas and aqueous phases creatine has the highest E_{HOMO}, whereas creatinine has the lowest value. On the other hand, creatinine has the lowest E_{LUMO} and ΔE values in both phases.

To place this in context, any effort to correlate the calculated E_{HOMO}, E_{LUMO} and ΔE values of the compounds with the experimentally observed inhibition efficiency is not fruitful. It is inherently difficult to establish a straightforward relationship or derived direct trend vis-à-vis the inhibition performance of these inhibitors.

Table 1. Calculated electronic properties of two inhibitors

Parameters	Phase[b]	Creatine	Creatinine
IE (%)[a]		90	89
E_{HOMO} (eV)	G	-6.247	-6.603
	A	-6.336	-6.379
E_{LUMO} (eV)	G	-0.782	-1.407
	A	-0.409	-1.287
ΔE (E_L-E_H) (eV)	G	5.465	5.196
	A	5.927	5.092
μ (D)	G	2.844	6.539
	A	5.197	9.965
ω	G	2.261	3.087
	A	1.919	2.885
χ	G	3.515	4.005
	A	3.373	3.833
η	G	2.733	2.598
	A	2.964	2.546
S	G	0.183	0.192
	A	0.169	0.196
ΔN	G	-0.208	-0.124
	A	-0.215	-0.160

[a] Ref. [5]
[b] G, gas phase ($\varepsilon = 1.0$); A, aqueous phase ($\varepsilon = 78.5$)

The reactivity of nucleophiles is typically quantified using the ω value; a lower value indicates a more reactive nucleophile. Conversely, a high value of ω is indicative of a good electrophile. With regard to this issue, creatinine functions as an effective electrophile in both phases. The energy disparity of a hard molecule is significantly larger than that of a soft molecule. It is observed that soft molecules exhibit a heightened degree of reactivity compared to their harder counterparts. This is attributed to the fact that they are capable of readily offering electrons to an acceptor, a phenomenon that is absent in their hard counterparts. It can be observed that creatinine represents the least rigid molecule under consideration. A comparison of the chemical hardness values with the energy gaps reveals a similar trend, with creatinine exhibiting the lowest value.

It should be noted that dipole moment (μ) is another parameter that predicts the polarized nature of the molecule; however, the exact relationship between this and inhibition efficiency is not entirely clear. It has been postulated that the efficiency of the inhibitor increases in proportion to the growth in the total dipole moment of the compound. This theoretical study has demonstrated that creatinine in an aqueous phase, despite lacking any discernible regularity, exhibits a high value of dipole moment.

The interaction of an inhibitor molecule with a bulk metal results in electrons flowing from the lower electronegative molecule to the higher electronegative metal until a state of chemical potential equilibrium is reached. The combination of a copper system and an inhibitor will result in the flow of electrons from the lower χ (inhibitor) to the higher χ (Cu). This transfer of charge will continue until the chemical potentials of both in situ entities are equalized.

The fraction of the transferred electron, ΔN, has been estimated for each molecule and is listed in Table 1. It has been established that an increase in the electron-donating ability of the molecules under consideration leads to an enhancement in the efficiency of the inhibition process, with the result that the ΔN value falls below 3.6 [14]. A larger proportion of electrons transferred is typically observed in creatine molecule, where its value in aqueous phase being identified as the greatest. In light of the aforementioned observations, it is evident that there is no discernible correlation between this order and inhibition efficiency values. Indeed, a systematic discrepancy is evident between the theoretical and experimental results, precluding a meaningful assessment of the efficacy of the order in question. The data set forth has demonstrated that ΔN is considerably smaller than 3.6 for all the considered cases. This conclusion is also supported by the results of a recent felicitous theoretical study [15].

4. Conclusion

The compatibility of the selected method with experimental values in literature provides evidence of the conformability of the method and the selected basis set for the optimization of inhibitor structures. However, the evaluation of molecular electronic parameters (ionization potential, electron affinity, chemical hardness, etc.) revealed no correlation between these parameters and the experimentally determined inhibition efficiency of creatine and creatinine compounds, tested as corrosion inhibitors for copper in sodium hydroxide solution. Nevertheless, the principal conclusion of this study is that commonly employed theoretical methodologies for predicting the correlation between molecular electronic properties and the inhibition efficiency of corrosion inhibitors have been shown to yield some degree of success. However, these same methodologies appear to lack the capacity to accurately predict the protective behavior of such compounds on metal surfaces in a corrosive environment. The relatively modest outcome can be attributed to the fact that DFT calculations are not yet feasible at the solid/water interface, which is imperious in such inhibitor studies. Since the development of an accessible computational model to describe solvent and electrified interfaces remains an arduous challenge, we envisage a range of future research studies that would be worth pursuing in this rapidly advancing field of research.

Author Contribution Statement

Conceptualization, G.G, S.B.; methodology, investigation, writing, review & editing, G.G. All authors have read and agreed to the published version of the manuscript.

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