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Theoretical Study of a New Group of Corrosion Inhibitors.

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ABSTRACT

The adsorption mechanism and inhibition performance of two aminobenzene derivatives such as 4-methylbenzene-1,2-diamine (AMPA) and Benzene-1,2-diamine (BD) were investigated as corrosion inhibitors for copper in 2.0 HNO_3 using density functional theory (DFT) at the B3LYP/6-31G(d,P) basis set level in order to investigate the relationship between their molecular and electronic structure and inhibition efficiency. The quantum chemical properties such as E_{HOMO} (highest occupied molecular orbital energy), E_{LUMO} (lowest unoccupied molecular orbital energy), energy gap (ΔE), dipole moment (μ), hardness (η), softness (S), the absolute electronegativity (χ), the fractions of electrons transferred (ΔN) and the electrophilicity index (ω) were calculated. The relation between the inhibition efficiency and quantum chemical parameters have been discussed in order to elucidate the inhibition mechanism of this compounds.

Keywords: Aminobenzene, Inhibitor, Corrosion, Copper, HNO_3, DFT.

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INTRODUCTION

An important method of protecting metallic materials against deterioration due to corrosion is by the use inhibitors. Organic compounds have become widely accepted as effective corrosion inhibitors in various media. Most of the organic inhibitors containing nitrogen, oxygen, sulfur atoms and multiple bonds in their molecules facilitate adsorption on the metal surface [1]. Researchers have concluded [2-27] that adsorption depends mainly on the physicochemical properties of the inhibitor group, such as functional groups, electronics density at the donor atom [2], π-orbital character, and the molecular electronic structure [28]. The relationship between the organic compound structures, the molecular adsorption processes and their inhibitive efficiency on metals has attracted intensive research on inhibitor compounds. In this regard, the theoretical study of the corrosion inhibition processes has not been widely studied due to the complexity of quantum mechanics computations. The large number of interactions due to the atoms of metallic surface, inhibitor molecules and solvent molecules increases the hardware requirements to do all electron calculations.

The density functional theory (DFT) [29] has been found to be successful is providing insights into the chemical reactivity and selectivity, in terms of global parameters such as the energies of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO}, dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), the global electrophilicity (ω), the fraction of electrons transferred (ΔN) and the total energy (TE). The chemical structures of the compounds studied are given in Fig 1.
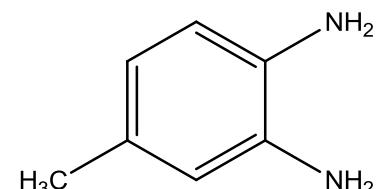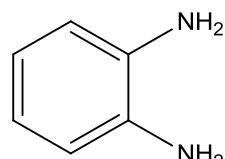
4-methylbenzene-1,2-diamine (AMPA)   **Benzene-1,2-diamine (BD)**

Figure 1: The molecular structures of the investigated inhibitors.

Quantum Chemical Calculations

Complete geometrical optimizations of the investigated molecules are performed using DFT (density functional theory) with the Beck's three parameter exchange functional along with the Lee-Yang-Parr nonlocal correlation functional (B3LYP) [30-32] with 6- 31G* basis set is implemented in Gaussian 03 program package [33]. This approach is shown to yield favorable geometries for a wide variety of systems. This basis set gives good geometry optimizations. The geometry structure was optimized under no constraint. The following quantum chemical parameters were calculated from the obtained optimized structure: The highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO}, dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), global softness (σ), ionization potential (I), the global electrophilicity (ω), the fraction of electrons transferred (ΔN) and the total energy (TE).

RESULTS AND DISCUSSION

The inhibition of copper using substituted aminobenzene as corrosion inhibitors were investigated experimentally. Table 1 indicates clearly a decrease in the corrosion rate in the presence of AMPA and ABT. This effect is hugely marked at higher concentration of inhibitors. The inhibitive action is more explicit by η_{WL}% data which increases with inhibitor concentration to reach 50.6% for DB, 66.9% for AMPA.

Table 1: Summarized the inhibition efficiency (η_{WL}%) obtained by addition of AMPA and ABT at different concentrations on the corrosion of copper in 2.0 M HNO$_3$ solution determined by potentiodynamic polarization [34].

	Conc (M)	C_R (mg cm^{-2} h^{-1})	η_{WL} (%)
HNO$_3$	2.0	1.780	----
	1×10^{-3}	0.878	**50.6**
	5×10^{-4}	0.956	46.3
DB	1×10^{-4}	1.111	37.6
	5×10^{-5}	1.290	27.5
	1×10^{-5}	1.537	13.6
	1×10^{-3}	0.590	**66.9**
	5×10^{-4}	0.654	63.3
AMPA	1×10^{-4}	0.821	53.9
	5×10^{-5}	1.022	42.6
	1×10^{-5}	1.454	18.3

In computational chemistry tools, the DFT offers the fundamentals for interpreting multiple chemical concepts used in different branches of Chemistry. In order to explore the theoretical-experimental consistency, quantum chemical calculations were performed with complete geometry optimizations using standard Gaussian-03 software package [33]. Geometry optimization were carried out by B3LYP functional at the 6-31G (d,p) basis set and at the density functional theory (DFT) level. Recently, Density functional theory (DFT) has been used to analyze the characteristics of the inhibitor/ surface mechanism and to describe the structural nature of the inhibitor in the corrosion process [35,36]. Furthermore, DFT is considered a very useful technique to probe the inhibitor/surface interaction as well as to analyze the experimental data. The results of the geometry optimization of the compounds AMPA and DB are presented in Figure 2.
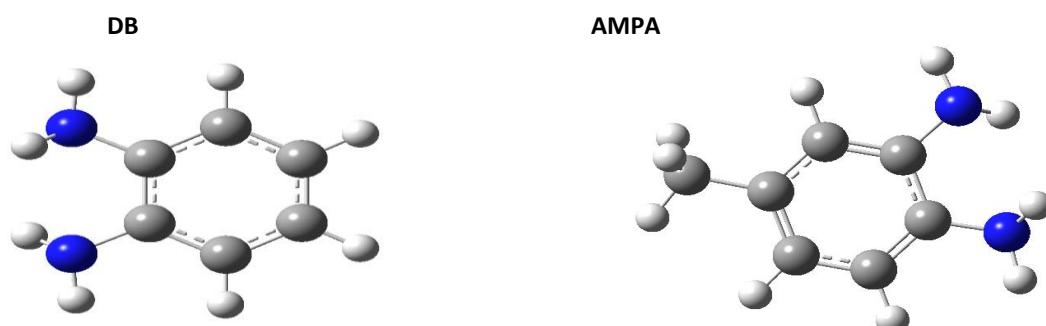

Figure 2: Optimized molecular structure of AMPA and DB by B3LYP/6-31G (d,p).

Density functional theory (DFT) [37] has been quite successful in providing theoretical basis for popular qualitative chemical concepts like electronegativity (χ), hardness (η), softness(S). According to Koopman's theorem [38] the ionization potential (IE) and electron affinity (EA) of the inhibitors are calculated using the following equations and hence χ and η are calculated.

$$I = - E_{HOMO} \tag{1}$$

$$A = - E_{LUMO} \tag{2}$$

The higher HOMO energy corresponds to the more reactive molecule in the reactions with electrophiles, while lower LUMO energy is essential for molecular reactions with nucleophiles [39].

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

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

The global softness(S) is the inverse of the global hardness [40].

$$S = \frac{1}{\eta} \tag{5}$$

Electronegativity, hardness and softness have proved to be very useful quantities in the chemical reactivity theory. The electronegativity of the inhibitor molecules is lower than the bulk iron. Hence, electron move from the molecules with lower electronegativity (inhibitor compound) toward that of a higher value (metal surface) until the equilibrium in chemical potential is reached.

The global electrophilicity index (ω), introduced by Parr [41], and calculated using the electronic chemical potential and chemical hardness is given by

$$\omega = \frac{\mu^2}{2\eta} \tag{6}$$

According to the definition, this index measures the propensity of chemical species to accept electrons [42]. A good, more reactive, nucleophile is characterized by lower value of ω; and conversely a good electrophile is characterized by a high value of ω. This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge ΔN from the environment.

According to Pearson theory [40] the fraction of transferred electrons (ΔN) from the inhibitor molecule to the metallic atom can be calculated. For a reaction of two systems with different electronegativities (as a metallic surface and an inhibitor molecule) the following mechanism will take place: the electronic flow will occur from the molecule with the lower electronegativity toward that of higher value, until the chemical potentials are the same. For the calculation the following formula was used [43].

$$\Delta N = \frac{\chi_{Cu} - \chi_{inh}}{2(\eta_{Cu} + \eta_{inh})} \tag{7}$$

In order to calculate the fraction of electrons transferred, a theoretical value for the electronegativity of bulk copper was used χ_{Cu}= 4.48 eV/mol [43], and a global hardness of η_{Cu} = 0 eV/mol by assuming that for a metallic bulk $I = A$ [44] because they are softer than the neutral metallic atoms.

According to the simple charge transfer model for donation and back-donation of charges proposed recently by Gomez et al., [45] an electronic back-donation process might be occurring governing the interaction between the inhibitor molecule and the metal surface. The concept establishes that if both processes occur, namely charge transfer to the molecule and back-donation from the molecule, the energy change is directly proportional to the hardness of the molecule, as indicated in the following expression.

$$\Delta E_{Back-donation} = -\frac{\eta}{4} \tag{8}$$

The ΔE Back-donation implies that when $\eta > 0$ and ΔE Back-donation < 0 the charge transfer to a molecule, followed by a back-donation from the molecule, is energetically favored. In this context, hence, it is possible to compare the stabilization among inhibiting molecules, since there will be an interaction with the same metal, then, it is expected that it will decrease as the hardness increases.

In Fig. 3, we have presented the frontier molecule orbital density distributions of the studied compounds: HOMO (right); LUMO (left). Analysis of Fig. 3 shows that the distribution of two energies HOMO and LUMO, we can see that the electron density of the HOMO location in the aminobenzene was distributed almost of the entire molecules, while the density LUMO was distributed of the amino moiety.

HOMO   **LUMO**

AMPA   **DB**
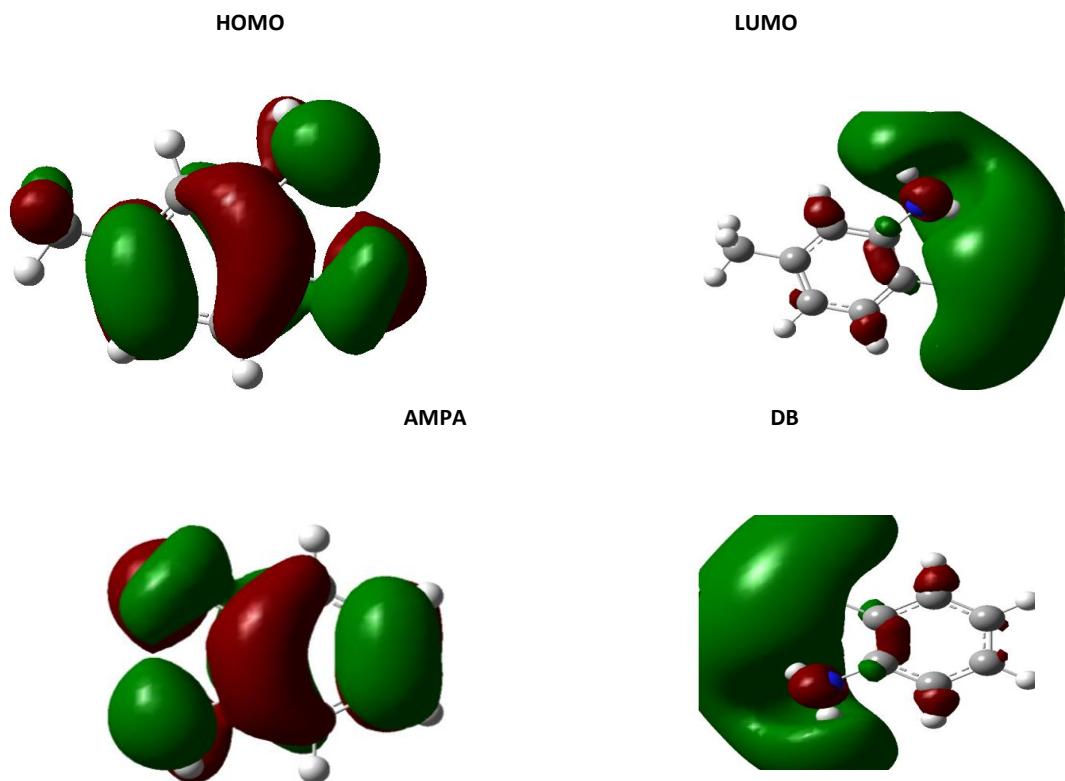
Figure 3: Schematic representation of HOMO and LUMO molecular orbital of studied molecules.

Table 2: Calculated quantum chemical parameters of the studied compounds.

Quantum parameters	DB	AMPA
E_{HOMO} (eV)	-5.39753	-5.28235
E_{LUMO} (eV)	-0.40083	-0.3785
ΔE gap (eV)	4.99671	4.90385
μ (debye)	1.21250	0.9163
$I = -E_{HOMO}$ (eV)	5.39753	5.28235
$A = -E_{LUMO}$ (eV)	0.40083	0.3785
$\chi = \dfrac{I+A}{2}$ (eV)	2.89918	2.83042
$\eta = \dfrac{I-A}{2}$ (eV)	2.49835	2.45192
$\sigma = \dfrac{1}{\eta}$	0.40026	0.40784

$\omega = \dfrac{\mu^2}{2\eta}$	0.294225	0.171214
$\Delta E_{Back-donation} = -\dfrac{\eta}{4}$	-0.62459	-0.61298
$\Delta N = \dfrac{\chi_{Cu} - \chi_{inh}}{2\left(\eta_{Cu} + \eta_{inh}\right)}$	0.316373	0.336385
TE (eV)	-9329.42592	-10331.46032

The inhibition effect of inhibitor compound is usually ascribed to adsorption of the molecule on metal surface. There can be physical adsorption (physisorption) and chemical adsorption (chemisorption) depending on the adsorption strength. When chemisorption takes place, one of the reacting species acts as an electron pair donor and the other one act as an electron pair acceptor. The energy of the highest occupied molecular orbital (E_{HOMO}) measures the tendency towards the donation of electron by a molecule [46]. High values of E_{HOMO} have a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy, empty molecular orbital. Increasing values of E_{HOMO} facilitate adsorption and therefore enhance the inhibition efficiency, by influencing the transport process through the adsorbed layer. Therefore, higher values of E_{HOMO} indicate better tendency towards the donation of electron, enhancing the adsorption of the inhibitor on mild steel and therefore better inhibition efficiency. E_{LUMO} indicates the ability of the molecule to accept electrons. The binding ability of the inhibitor to the metal surface increases with increasing of the HOMO and decreasing of the LUMO energy values. Table 2 represents the total energy and calculated energy levels in (eV) of the HOMO, LUMO and energy gap of the investigated molecules.

According to the frontier molecular orbital theory (FMO) of chemical reactivity, transition of electron is due to interaction between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of reacting species [47]. E_{HOMO} is a quantum chemical parameter which is often associated with the electron donating ability of the molecule. High value of E_{HOMO} is likely to a tendency of the molecule to donate electrons to appropriate acceptor molecule of low empty molecular orbital energy [48]. The inhibitor does not only donate electron to the unoccupied d orbital of the metal ion but can also accept electron from the d-orbital of the metal leading to the formation of a feed back bond. According to our result, the highest E_{HOMO} value -5.28235 (eV) of AMPA indicates the better inhibition efficiency.

It has also been found that an inhibitor does not only donate an electron to the unoccupied d orbital of the metal ion but can also accept electrons from the d orbital of the metal leading to the formation of a feedback bond. Therefore, the tendency for the formation of a feedback bond would depend on the value of E_{LUMO}. The lower the E_{LUMO}, the easier is the acceptance of electrons from the d orbital of the metal [49]. Based on the values of E_{LUMO}, this parameter presents no correlation between the experimental results and theoretical calculations.

The energy gap, ($\Delta E = E_{LUMO} - E_{HOMO}$) is an important parameter as a function of reactivity of the inhibitor molecule towards the adsorption on the metallic surface. As ΔE decreases, the reactivity of the molecule increases leading to increase in the η_{WL}% of the molecule. Lower values of the energy difference will render good inhibition efficiency, because the energy to remove an electron from the last occupied orbital will be low [50]. Reportedly, excellent corrosion inhibitors are usually organic compounds which not only offer electrons to unoccupied orbital of the metal but also accept free electrons from the metal [51]. A molecule with a low energy gap is more polarizable and is generally associated with the high chemical activity and low kinetic stability and is termed soft molecule [52]. Soft molecule is more reactive than a hard molecule because a hard molecule has a large energy gap. The results as indicated in table 2 shows that inhibitor AMPA has the lowest energy gap, this means that the molecule could have better performance as corrosion inhibitor.

Ionization energy is a fundamental descriptor of the chemical reactivity of atoms and molecules. High ionization energy indicates high stability and chemical inertness and small ionization energy indicates high

reactivity of the atoms and molecules [53]. The low ionization energy 5.28235 (eV) of AMPA indicates the high inhibition efficiency.

Absolute hardness and softness are important properties to measure the molecular stability and reactivity. It is apparent that the chemical hardness fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has a large energy gap and a soft molecule has a small energy gap [54]. In our present study AMPA with low hardness value 2.45192 (eV) compared with BD, have a low energy gap. Normally, the inhibitor with the least value of global hardness (hence the highest value of global softness) is expected to have the highest inhibition efficiency [55]. For the simplest transfer of electron, adsorption could occur at the part of the molecule where softness (σ), which is a local property, has a highest value [56]. AMPA with the softness value of 0.40784 has the highest inhibition efficiency.

The dipole moment (μ in Debye) is another important electronic parameter that results from non uniform distribution of charges on the various atoms in the molecule. The high value of dipole moment probably increases the adsorption between chemical compound and metal surface [57]. The energy of the deformability increases with the increase in μ, making the molecule easier to adsorb at the Cu surface. The volume of the inhibitor molecules also increases with the increase of μ. This increases the contact area between the molecule and surface of iron and increasing the corrosion inhibition ability of inhibitors. In our study, there is no direct relationship between the $\eta_{WL}\%$ and the dipole moment.

According to Sanderson's electronegativity equalization principle [58], BD with a high electronegativity quickly reaches equalization and hence low reactivity is expected which in turn indicates low inhibition efficiency. The table 2 shows the order of electronegativity as BD > AMPA. Hence an increase in the difference of electronegativity between the metal and the inhibitor is observed in the order AMPA > BD. The electrophilicity index, ω, shows the ability of the inhibitor molecules to accept electrons. It is a measure of the stabilization in energy after a system accepts additional amount of electron charge from the environment [59]. In our present study, AMPA is the strongest nucleophile while BD is the strongest electrophile.

The number of electrons transferred (ΔN) was also calculated depending on the quantum chemical method as in Eq. (7). Values of ΔN showed that the inhibition efficiency resulting from electron donation agreeing with Lukovits's study [52]. If $\Delta N < 3.6$, the inhibition efficiency increases by increasing electron-donating ability to the metal surface and the order by which the ability of these inhibitors to donate electrons to the metal surface increase is: AMPA > BD. The values of ΔN indicate trends within a set of molecules, but their absolute value might not correspond to reality. ΔN values are not exactly the number of electrons leaving the donor and entering the acceptor molecule. The expression ''electron-donating ability'' is more adequate than ''number of transferred electrons'' [60]. The calculated ΔE back-donation values for both, inhibitors are listed. The order followed is: AMPA > BD, which indicates that back-donation is favoured for the AMPA, which is the best inhibitor.

The total energy calculated by quantum chemical methods is also a beneficial parameter. The total energy of a system is composed of the internal, potential, and kinetic energy. Hohenberg and Kohn [39] proved that the total energy of a system including that of the many body effects of electrons (exchange and correlation) in the presence of static external potential (for example, the atomic nuclei) is a unique functional of the charge density. The minimum value of the total energy functional is the ground state energy of the system. The electronic charge density which yields this minimum is then the exact single particle ground state energy. In our study the total energy of the best inhibitor AMPA is equal to -10331.46032 eV, this value is lower than that of the compound BD.

CONCLUSIONS

Using the DFT/B3LYP method, the inhibition efficiency of aminobenzene derivatives is investigated that leads to the following conclusions:

- The quantum parameter shows that the HOMO energies are correlated to the inhibition efficiency. High value of E_{HOMO} is likely to indicate a tendency of the inhibitor to donate electrons to appropriate

acceptor molecule, Cu surface, of low empty molecular orbital energy. The inhibition efficiency increases with the increasing of the HOMO energy values.

- The separation energy, ΔE, which is a function of reactivity, is correlated to the inhibition efficiency of studied inhibitors. As, ΔE decreases, the reactivity of the inhibitor towards the copper surface increases.
- A good correlation is found between the total energy and IE. The inhibition efficiency increases with increasing the dipole TE.
- Also, the softness and hardness are correlated to the inhibition efficiency. The inhibition efficiency increases with increasing the softness value.
- There is no direct relationship between the inhibition efficiency and the dipole moment.
- AMPA has the highest inhibition efficiency because it had the highest HOMO energy and ΔN values and lowest energy gap it was most capable of offering electrons and it could have a better performance as corrosion inhibitor.

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