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INHIBITIVE ACTION OF IMIDAZOLES FOR COPPER CORROSION IN SULFURIC ACID MEDIUM

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ABSTRACT

The corrosion inhibition of copper in the presence of 10^{-3} M of imidazole derivatives; Imidazole (IM), 2-Methyle imidazole (MIM), Benzimidazole (BIM) has been investigated in 1.0 M H_2SO_4 solution using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Relationship between molecular structure and their inhibition efficiency was elucidated by quantum chemical calculations using the density functional theory (DFT) at the B3LYP/6-31+G(d,p) level. Inhibition efficiency of these compounds which has been evaluated via experimental methods was accorded with reported theoretical ones, and following the same order as BIM > MIM > IM.

Indexing terms/Keywords

Keywords: Imidazole; Copper; Density functional theory; Corrosion inhibitors.

Academic Discipline And Sub-Disciplines

Chemical Physics

SUBJECT CLASSIFICATION

Experimental and therical chemistry

TYPE (METHOD/APPROACH)

Provide examples of relevant research types, methods, and approaches for this field: E.g., Historical Inquiry; Quasi-Experimental; Literary Analysis; Survey/Interview

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INTRODUCTION

The study of copper corrosion and their inhibition by organic inhibitors in acid solution is a subject of practical significance, because, the copper is widely used in various industrial operations, its used in microelectronics, fabrication of heat exchanger tubes and cooling water systems, due to its high thermal, electrical conductivities, low cost and malleability [1-4].

Among acid solutions, sulfuric acid, it's often used as a pickling acid for copper and its alloys. The main goal is undesirable corrosion products. To make secure from attack of acid, the use of organic compounds containing nitrogen as corrosion inhibitors is widely spread for many metals and alloys [5,6], little is known their functions due to the complexity of the process [7]. Corrosion inhibition of copper can be achieved through the modification of its interface by forming self assembled ordered ultrathin layers of organic inhibitors. Commonly used inhibitors for copper corrosion are toxic compounds that should be replaced with the new ecofriendly inhibitors. Most of the inhibitors are organic compounds and their derivatives such as imidazole [8-15].

The aim of the present work in this paper is to investigate the effect of some imidazole namely; 1-3 imidazole (IM), 2-methyl 1-3 imidazole (MIM), benzimidazole (BIM), on the corrosion behavior of copper in sulfuric acid solution, by use of electrochemical methods and theoretical study.

Experimental

The electrochemical measurements were carried out in a conventional three-electrode electrochemical cell consisting of platinum electrode as auxiliary electrode, a saturated calomel electrode (SCE) as reference, and copper metal as working electrode. The copper electrode was a disc of pure copper of surface area 0.35 cm^2; before measurements it was polished successively with emery paper up to 1200 grade, then rinsed thoroughly with acetone and bidistilled water and maintained at its free potential of corrosion for 30 min. The scan rate for potentiodynamic polarization study was 60 mV/min. The potential ranged from -800 to +500 mV/SCE. Impedance measurements were carried out in frequency range from 100 kHz to 40 mHz with an amplitude of 10 mV peak-to-peak using ac signals at open circuit potential. All electrochemical measurement were preferment using VoltaLab potentiostat/galvanostat (LG304) piloted by VoltaMaster 4 software. All experiments were carried out in aerated solution at the constant temperature (25 ± 0.1 °C).

Computational study

The purpose of this study is to provide information about the electron configuration of these organic inhibitors by quantum chemical calculations and to investigate the relationship between molecular structure and inhibition efficiency. The quantum chemical calculations have been widely used to interpret reaction mechanisms with the experimental results as well as to resolve chemical ambiguities [15]. The geometrical optimization and computation of the energies of the molecules, E_{HOMO}, E_{LUMO}, energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$), dipole moment and atomic charges, was been performed by use of Density Functional Theory (DFT) with the Beck's three-parameter exchange functional and the Lee–Yang–Parr nonlocal correlation functional (B3LYP) with the 6-31+G(d,p) basis set, as implemented in the Gaussian 03 software package for Windows via dual core 2.40 GHz processor [17]. All quantum calculations were conducted in vacuum phase.

Results and Discussion

1. Electrochemical studies

1.1. Potentiodynamic polarization measurements

Polarization measurements are commonly accepted to provide the relevant information about the kinetics of electrochemical corrosion parameters. Fig. 1, manifestation of cathodic and anodic polarization curves recorded for copper in 1.0 M H_2SO_4 solution at 10^{-3} M of IM, MIM and BIM. As we can see in Fig. 1, it is obvious that imidazole derivatives causes a decrease in current density as a consequence of the blocking effect of inhibitors on the metal surface. Dissolution of copper in sulfuric acid is described by the following two consecutive steps:

$$Cu \rightarrow Cu^{+}_{ads} + e^{-} \qquad (1)$$

$$Cu^{+}_{ads} \rightarrow Cu^{2+} + e^{-} \qquad (2)$$

where Cu^{+}_{ads} is an adsorbed species at the copper surface and does not diffuse into the bulk solution [18].

From Fig. 1, the anodic curves during the oxidative reaction in inhibitor free solution shown an apparent-Tafel region, which can due to the dissolution of copper into Cu^{+} [18]. However, in the same region and in presence of imidazole derivatives, as we can see, the pic of oxidation of copper was disparate. It is likely that the inhibitor molecules have adsorbed onto the copper surface, which could decrease the oxidation rate of the initial step of copper corrosion [19-22]. Therefore, it might be difficult for the corrosion to proceed to the next step [23], but the charge transfer remains as a general mechanism to anodic dissolution of copper.

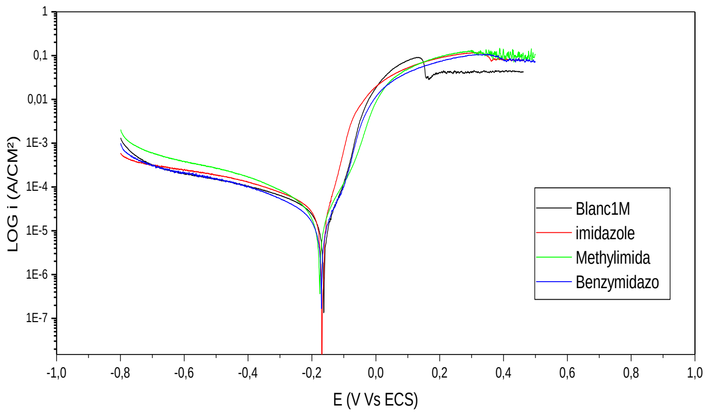

Figure 1 Potentiodynamic polarization curves for copper in 1.0 M H_2SO_4 containing different imidazole derivatives at 10^{-3} M.

We note that cathodic polarization of copper in absence or in presence of all imidazole derivatives in sulfuric acid solution show similar behavior, in other words, these compounds has not affecting the cathodic reaction mechanism of copper. The cathodic polarization can attributed to a diffusion current controlled by the reduction of dissolved oxygen. The cathodic corrosion reaction in an aerated sulfuric acid solution can be expressed either by a direct four electrons transfer as shown by the following equation:

$$O_2 + 4H^+ + 4e- \rightarrow 2H_2O \qquad (3)$$

or by two consecutive 2e- steps involving a reduction to hydrogen peroxide first

$$O_2 + 2H^+ + 2e- \rightarrow H_2O_2 \qquad (4)$$

followed by a further reduction [24].

$$H_2O_2 + 2H^+ + 2e- \rightarrow 2H_2O \qquad (5)$$

The useful corrosion kinetic parameters namely the corrosion potential (E_{corr}), anodic Tafel slope (b_a) and corrosion current density (I_{corr}), for inhibited solution and inhibitor free solution are obtained from the polarization curves summarized in Table 1. It was not possible to evaluate the cathodic Tafel slope (b_c) because a hump was present at potential close to E_{corr} [25]. The inhibition efficiency was calculated from the following equation:

$$E_I(\%) = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100 \qquad (6)$$

where I_{corr} and I'_{corr} are corrosion current densities without and with inhibitors respectively, as determined by extrapolation of anodic Tafel lines to corrosion potential [26].

Table 1 Electrochemical parameters and inhibition efficiency of copper in 1.0 M H_2SO_4 medium in the absence and presence of 10^{-3} M of imidazole compounds

Medium	E_{corr} (mV vs. SCE)	b_a (mV.dec^{-1})	I_{corr} (µA.cm^{-2})	E_I (%)
Blank	-131	65	33	-
IM	-154	66	20	40
MIM	-163	64	16	51
BIM	-160	68	12	62

Thus, the presence of Imidazole compounds at 10^{-3} M leads to decrease in the values of I_{corr}, which was particularly significant in the case of BIM.

1.2. Electrochemical impedance spectroscopy (EIS) studies

Electrochemical impedance spectra of copper in absence and in presence of IM, MIM and BIM at 10^{-3} M in 1.0 M H_2SO_4 after 30 min of immersion are depicted as Nyquist plots in Fig. 2. This figure shows that the impedance plots consist of a single capacitive semi-circle, mainly, due to charge transfer processes and double ionic layers property [27]. The increase in the size of the semi-circle in presence of the inhibitors indicates that a barrier gradually forms on the copper surface.

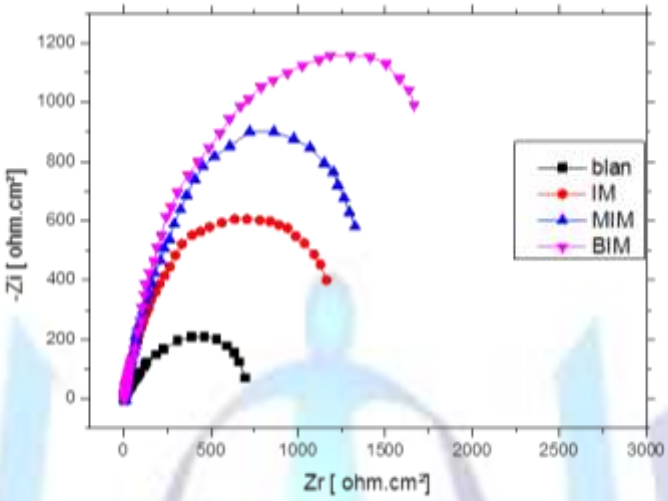

Figure 2 Impedance diagram of copper in 1.0 M H_2SO_4 without and with the addition of imidazole compounds at 10^{-3}M

The charge-transfer resistance (R_t) values are calculated from the difference in impedance at lower and higher frequencies [28]. To obtain the double layer capacitance (C_{dl}) the frequency at which the imaginary component of the impedance is maximal ($-Z_{max}$) is found as represented in equation:

$$C_{dl} = \frac{1}{\omega . R_t} \qquad (7)$$

where $\omega = 2\pi f_{max}$, is frequency in rad.s^{-1} and f_{max} is the frequency in Hz. The percentage of inhibition efficiency (E_t(%)) was calculated from the impedance measurements using the following relation:

$$E_t(\%) = \frac{R'_t - R_t}{R'_t} \times 100 \qquad (8)$$

where R_t' and R_t are the charge transfer resistance values with and without inhibitor, respectively. Table 2 reported different values of electrochemical parameter deduced from EIS study.

Table 2 Impedance parameters for copper in 1.0 M H_2SO_4 with and without addition of imidazole compounds at 10^{-3} M, and the corresponding inhibition efficiency

Medium	R_t ($\Omega.cm^2$)	f_{max} (Hz)	C_{dl} ($F.cm^{-2}$)	E_t (%)
Blank	749	0.51	0.0004169	-
IM	1330	3.49	0.0000343	43
MIM	1600	3.48	0.0000285	53
BIM	2035	2.81	0.0000278	63

Increasing R_t values in presence of Imidazole compounds, suggesting decrease of the corrosion rate, as the R_t value is a measure of electron transfer across the surface, and inversely proportional to the corrosion rate. The decrease in the C_{dl} values could be attributed to the adsorption of the molecules of inhibitors at the metal surface [29]. The data shown in table 2 indicate that addition of imidazole compounds leads to increase of the charge transfer resistance which is associated with a decrease of double layer capacitance. E_t(%) varied in the sequence: IM < MIM < BIM. The inhibition efficiency obtained from EIS measurement are close to those deduced from polarization.

2. Computational Study

To investigate the relationship between molecular structures of the inhibitor and their inhibition effect, quantum chemical molecular calculations have proved to be a powerful tool for studying corrosion inhibition mechanism. Certain quantum chemical parameters such as the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy gap ($\Delta E_{LUMO - HOMO}$), net atomic charges and the dipole moment (μ) can be related to the interactions of metal-inhibitor [16,30]. The HOMO is the orbital that could act as an electron donor, where the corrosion rate decreases with increase in HOMO energy (less negative). The LUMO is the orbital that could act as the electron acceptor from the d orbital of the metal, so, the decrease of LUMO energy conduct to increase of inhibition efficiency of inhibitor. In the case of energy gap ($\Delta E_{LUMO - HOMO}$), its lower values involves the better corrosion inhibition because the excitation energy to remove an electron from the last occupied orbital will be low [31].

In this study, quantum chemical calculations were conducted by DFT method (B3LYP/6-31+G(d,p)). Fig. 3 shows the optimization energies of the studied imidazole derivatives and their optimized structures. As can be seen in Fig. 3 the lowest energy is calculated for the IM derivatives, MIM and BIM, respectively.

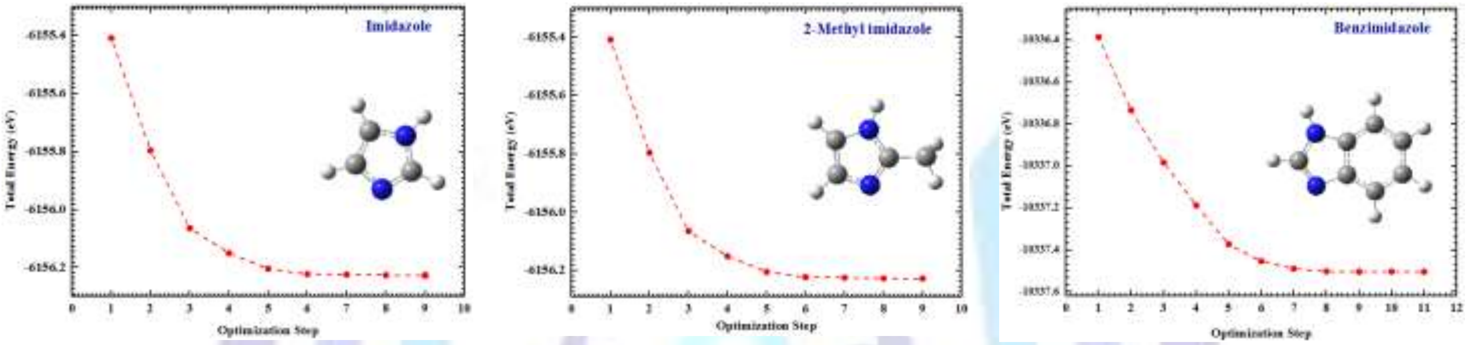

Figure 3 Optimization energy for imidazole derivatives and their optimized structures obtained by DFT method.

The E_{HOMO}, E_{LUMO}, energy gap (between LUMO and HOMO orbitals) and dipole moment values of studied imidazole compounds were listed in Table 3.

Table 3 HOMO and LUMO energies, energy gap ($\Delta E_{LUMO - HOMO}$) and dipole moment μ for IM, MIM and BIM obtained using DFT calculations.

Inhibitor	E_{HOMO} (eV)	E_{LUMO} (eV)	$\Delta E_{LUMO - HOMO}$ (eV)	μ (D)	EI (%)
IM	-9.415	-3.782	5.633	3.87	43
MIM	-9.252	-3.782	5.470	3.73	53
BIM	-9.633	-5.415	4.218	3.58	63

From the results of Table 3, we note that energy gap between LUMO and HOMO orbitals decrease in the order, IM > MIM > BIM, which causes the transfer of electrons from the highest occupied molecular orbital to lowest unoccupied molecular orbital becomes increasingly easy passing from IM to BIM where the inhibitory efficiency is maximum. Also, these results indicate that the charge transfer from the inhibitor to the metal took place easy from BIM to IM during the adsorption of the latter to the metal surface, according to the frontier molecule orbital theory (FMO) of chemical reactivity [32,33]. Decreasing dipole moment in the order, BIM < MIM < IM accompanying by an increasing in the inhibition phenomenon, which reveals that is no regular trend in the inhibition efficiency by increasing values of μ as was observed in previous studies [33,34]. These results agree with the experimental observations, which imply that BIM compound has better corrosion performance compared to the IM and MIM compounds. The relationship between corrosion inhibition efficiency (we used the EIS results) with gap energy and with dipole moment for imidazole compounds was plotted in Fig. 4. It is clear from the figure that the inhibition efficiency increased with the decreasing of gap energy and dipole moment values. In other hand, the efficiency inhibition of tested compounds was strongly depended to the dipole moment value as correlation coefficient was showed (R^2 = 0.999, Fig. 4(b)) against to gap energy (R^2 = 0.662, Fig. 4(b)). Thus, we can suggested that the interaction between inhibitors molecules and metallic surface was probably chemical interaction, as we found in another study carried out in parallel with this study.

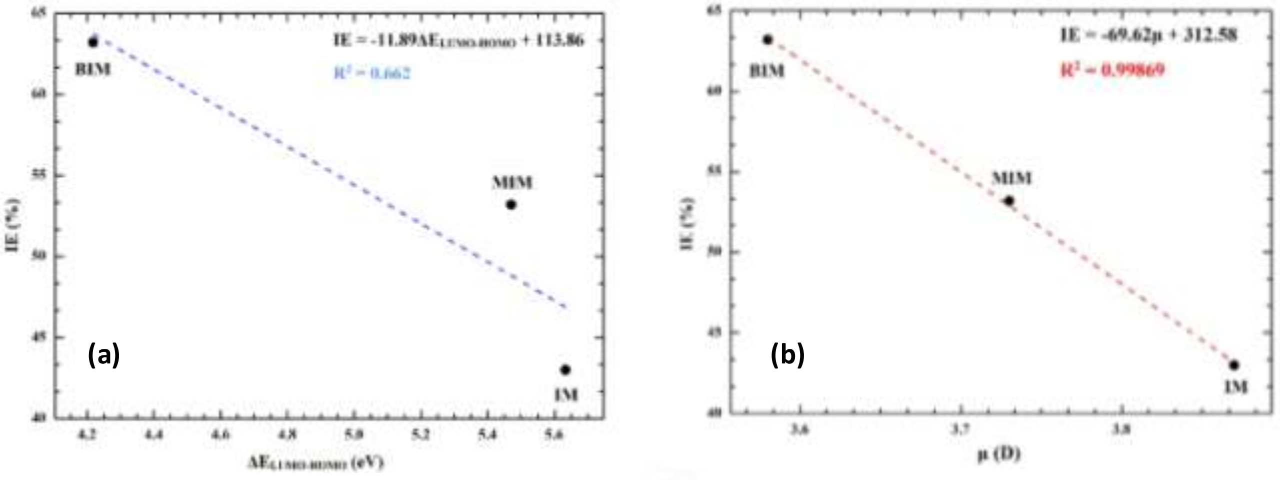

Figure 4 Correlation of gap energy (a) and dipole moment (b) with percentage inhibition efficiency for imidazole compounds.

For the imidazole derivatives, the nature of their molecular orbitals density distribution, HOMO and LUMO are presented in Fig. 5. It is well known in the literature that the nitrogen atom of the imidazole compounds is the reaction center for adsorption onto a metal surface [35]. As we can see the density of the HOMO and LUMO for the tree compounds were distributed al most of the entire molecules.

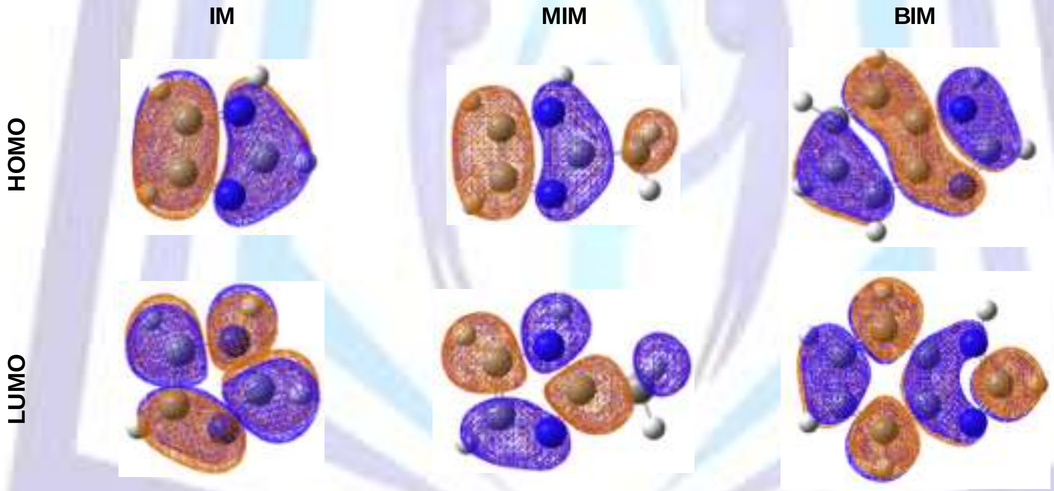

Figure 5 Molecular orbital plots for imidazole derivatives.

Furthermore, in order to confirm the adsorption centers of imidazole derivatives molecules when adsorbed on copper surface via chemical bond, the local site of these molecules were investigated by analysis of their charges distribution, which has an important role in chemical reaction and the physico-chemical properties of compounds [16].

IM **MIM** **BIM**

Figure 6 The numbering systems chosen for different atomic centers for each molecule.

In Fig. 6 we have shown the molecular structures of imidazole with the numbering systems chosen for different atomic centers for each molecule, and in Table 4, we listed the charge distribution calculated by the DFT methods on the backbone of each inhibitor molecule.

Table 4 Calculated Mulliken atomic charges for the three selected imidazole derivatives.

	Atom	**N1**	**C2**	**N3**	**C4**	**C5**	**C6**	**C7**	**C8**	**C9**
Inhibitor	**IM**	-0.354	0.094	-0.316	-0.070	-0.073				
	MIM	-0.386	0.523	-0.319	-0.035	-0.059	-0.795			
	BIM	-0.461	0.294	-0.336	0.289	-0.617	-0.195	-0.245	-0.370	0.693

As shown from Table 4 the net atomic charges are greater on the nitrogen atoms and low on the carbon atoms for the tested molecules excepting the C6 of methyl group in MIM, which can present another favorite site for adsorption. However, the larger electronic charge is obtained for the BIM derivative. Thus, these compounds can be adsorbed on the metal surface through donating their lone pair of electrons on nitrogen to the vacant d orbital of metal atom [36]. For BIM compound, it is important to acknowledge the contribution of the high electron density of the aromatic ring which is very rich in π electrons plays a key role in the inhibition process.

So from this charge analysis, it appears that the power of BIM inhibitor is due to their chemisorption on the surface of copper through the active centers such as aromatic ring.

Conclusion

From the obtained results, we can deduce the following conclusions:

- All investigated imidazole compounds (IM, MIM and BIM) have shown inhibiting properties for copper corrosion in 1 M sulfuric acid.
- The comparative study of the action of imidazole derivatives showed that the BIM compound is the best inhibitor of the proposed series (BIM > MIM > IM).
- Through the quantum chemical calculations, it was shown that calculated parameters were correlated with the experimental results and it was found that inhibition efficiency increased with the lower value of $\Delta E_{LUMO - HOMO}$ and dipole moment. Likewise. The maximum inhibitory power of BIM is mainly due to high electron density on the nitrogen atoms and the aromatic ring, which causes a significant adsorption of BIM on the metal surface.

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