Theoretical study for chromen azodyes derivative compounds as anti-corrosive

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Abstract. The anti-corrosive behaviour of some azo compounds derivatives, (a) 4,6,7-trimethyl-8-((2-nitrophenyl)diazenyl)-2H-chromen-2-one, (b) 2-((4,6,7-trimethyl-2-oxo-chromen-8-yl)diazenyl)benzoic acid, (c) 4,6,7-trimethyl-8-(phenyldiazenyl)-chromen-2-one, (d) 8-((2-hydroxyphenyl)diazenyl)-4,6,7-trimethyl-chromen-2-one and (e) 8-((2-methoxyphenyl)diazenyl)-4,6,7-trimethyl-chromen-2-one are investigated using density functional B3LYP/6-311G. Electronic properties such as; the highest occupied molecular orbital, the lowest unoccupied molecular orbital, the dipole moment, the softness, total energy and the total negative charge are calculated to find a relation between their structural properties and the inhibition efficiency. The calculated quantum chemical parameters correlated to the inhibition efficiency are measured. The results showed a good correlation between the experimental inhibition efficiency and the quantum chemical parameters.

1. Introduction
There are a wide range applications of azo compounds as: drugs delivery system [1–4], antibectrail agent [5–7], in solar cells application [8, 9] and as corrosion inhibitors for metals surface and alloy [10, 11]. Several studies; suggested that compounds such azocompounds containing oxygen, sulphur or nitrogen donor atoms, and a π-system show as active inhibitors [12–15]. It is evidenced that their activity toward corrosion inhibition increase by existence of heteroatoms and π system which easy to create in azocompounds. Interaction between metal surface and inhibitor agent is divided into two types; chemical or physical interactions. During the chemical adsorption, a coordination bond is formed when electrons of the organic inhibitors transferred to the vacant orbital of the metal. These compounds have the ability to generate new bond with metal surface by forming chemisorptions because they have electronegative group and conjugated bonds in the case of aromatic azo compounds, this lead to increase the ability of these material to form the chemisorption such as azoles [16–18]. Physicochemical feature of corrosion inhibitors plays an important role in the adsorption of the inhibitors on the metals surface [19–21]. The efficiency of inhibitors depend not only on functional groups of organic compounds and electrons density of donor atoms, but also, on the molecular electronic structure and ability of active site to form metallic complexes [22, 23]. The present work is aimed to investigate the calculations of structural properties of reported azocompounds with a view to relate structural properties of reported compounds to the inhibition efficiency [24].
2. Theorical method
The density functional theory (DFT) with the Becks three-parameter exchange functional along with the Lee-Yang-Parr nonlocal correlation functional (B3LYP) is used to perform complete geometrical optimization for the inhibitors molecules [25, 26]. These inhibitor molecules have been optimized using Gaussian 09 software (G09) with implementing 6-311G basis set [27]. The adsorption centers of the inhibitor molecules are obtained from the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Due to Koopmans theorem [28], the absolute electronegativity, and absolute hardness are related to ionization potential and electron affinity of any chemical system by the following relations,

\[ \chi = \frac{1}{2}(I + A). \]  

(1)

The difference between the lowest unoccupied molecular orbital energy (\(E_{\text{LUMO}}\)) and the highest occupied molecular orbital energy (\(E_{\text{HOMO}}\)) is the separation energy (energy gap),

\[ \Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}. \]  

(2)

The ionization energy and electron affinity are related to the HOMO and LUMO energies as,

\[ I = -E_{\text{HOMO}}, \quad A = -E_{\text{LUMO}}. \]  

(3)

The absolute hardness is given as

\[ \eta = \frac{1}{2}(I - A), \]  

(4)

and the softness \(\sigma\) is the inverse of the hardness

\[ \sigma = \frac{1}{\eta}. \]  

(5)

3. Results and Discussion
From the molecular structures Fig. (1), it is clear that the studied azo dyes compounds have the azo group (N=N) which has basic property due to the existence of lone pair of electrons on the two nitrogen atoms and the character of electron donating of the double bond. As mentioned azo compounds (a-e) have N=N group, subsequently, this group has ability to form complexes with metal ion.

M. Abdallah et al. have been investigated the experimental inhibition efficiency of the compounds a, b, c, d and e [24]. Their results are presented in Table. 1 with the results of the quantum chemical parameters obtained from our calculations. The inhibition efficiency of inhibitors (IE) can correlate with these quantum parameters such as separation energy (energy gap) \(\Delta E\), dipole moment \(\mu\), total negative charge TNC, total energy TE, softness \(\sigma\) and volume of molecules. The experimental results revealed that the inhibitors efficiency of azo dyes compounds will be in the order: Inhibitor e > Inhibitor d > Inhibitor c > Inhibitor b > Inhibitor a.

The calculation in this work suggested that the bond N_{15}=N_{16} in the compound (c) has (1.279 Å) bond length less than other bond length in the same compound which reveals azo double bond, in addition, C_{3−N_{15}} and C_{17−N_{16}} have bond lengths 1.411 Å and 1.428 Å respectively which further evidence to single bond. Same results observed in compounds a,b, d and e (see Table. 2). The \(\pi\) charge of the azo groups can enable the adsorption of the inhibitor in all cases.

The high values of densities on N_{15}, N_{16} and O_{14} of all compounds are shown in Table. 3 and they reveal that an adsorption center to the metal could be from the azo group and O atoms.

Inhibition efficiency is affected directly by the quantum parameters [29–32] such as the energies of frontier molecular orbitals \(E_{\text{HOMO}}\) and \(E_{\text{LUMO}}\). The electron providing ability of
Figure 1. Azo compounds derived from chromen-2-one.

Table 1. Presents theoretical parameters achieved from the calculations such as $E_{\text{HOMO}}$, $E_{\text{LUMO}}$, the separation energy, dipole moment, total energy, softness, volume of the molecules and the total negative charge. The Inhibition efficiency of mono azo dye compounds for corrosion of C-steel in 2M HCl solutions using weight loss method at 40 °C.

| Quantum parameters | Inhibitor (a) | Inhibitor (b) | Inhibitor (c) | Inhibitor (d) | Inhibitor (e) |
|--------------------|---------------|---------------|---------------|---------------|---------------|
| $E_{\text{HOMO}}$ (eV) | -6.239 | -6.010 | -5.772 | -5.603 | -5.546 |
| $E_{\text{LUMO}}$ (eV) | -2.829 | -2.633 | -2.397 | -2.289 | -2.252 |
| $\Delta E$ (eV) | 3.410 | 3.376 | 3.374 | 3.314 | 3.293 |
| $\mu$ (Debye) | 10.783 | 2.574 | 5.800 | 5.397 | 6.008 |
| $\sigma$ (softness) | 0.587 | 0.592 | 0.593 | 0.603 | 0.607 |
| Volume ($\text{cm}^3\text{ mol}^{-1}$) | 214.361 | 233.863 | 218.984 | 221.174 | 222.163 |
| TNC | -4.223 | -4.708 | -3.891 | -4.396 | -4.514 |
| IE* | 55.37 | 61.4 | 65.18 | 68.95 | 71.63 |

*Experimental data of inhibition efficiency (IE) obtained from Ref. [24].

Table 2. The calculated bonds length of compounds a, b, c, d and e.

| Inhibitor | $N_{15}=N_{16}$ Å | $C_{3}-N_{15}$ Å | $N_{16}-C_{17}$ Å |
|-----------|-----------------|-----------------|-----------------|
| a         | 1.27704         | 1.41235         | 1.43096         |
| b         | 1.27597         | 1.41157         | 1.43147         |
| c         | 1.27930         | 1.41176         | 1.42876         |
| d         | 1.28040         | 1.41196         | 1.41833         |
| e         | 1.28090         | 1.41222         | 1.41805         |
Figure 2. The molecular structures of antipyrine azodyes compounds optimized in G09 using density functional theory along with (B3LYP) and with implementing 6-311G basis set.

The inhibition efficiency increases with the decrease in the energy gap. The calculation in this work suggests that the compound (e) with the $\Delta E$ is 3.293 eV,

compounds increase by the high value of $E_{HOMO}$ because it evidence of molecules to donate the electron. In contrast, the $E_{LUMO}$ indicates the ability of the compound to receive electrons density. Decrease energy gap, $\Delta E$ (interaction between the $E_{HOMO}$ and $E_{LUMO}$) lead to decrease the ability of inhibitors due to deficient electron density that may transfer to the metals [33, 34].

It is obvious from the Table. 1, the inhibition efficiency increases with the decrease in the energy gap.
Table 3. Electron density on $N_{15}$, $N_{16}$ and $O_{14}$ atoms for a, b, c, d and e inhibitors.

| Inhibitor | $N_{15}$ | $N_{16}$ | $O_{14}$ |
|-----------|----------|----------|----------|
| a         | -0.254   | -0.298   | -0.399   |
| b         | -0.261   | -0.272   | -0.412   |
| c         | -0.276   | -0.303   | -0.410   |
| d         | -0.275   | -0.286   | -0.413   |
| e         | -0.275   | -0.286   | -0.414   |

literately this give evidence that compound (e) has highest reactivity and subsequently highest (IE). It is clear that the type of adsorption relay on the attraction between the metal and the electron on inhibitor. The sequence of increasing the inhibitors reactivity was as obey: compound (e) > compound (d) > compound (c) > Compound (b) > Compound (a). The reasons behind this are: (1) the presence of ortho methoxy group in compound (e) which an electron providing group will increase the electron density on this compound, compound (e) is more active than compound (d) due to the existence of hydroxyl group which behaves as donating group, but its donating ability is less than (O-CH$_3$). The compound (c) has no substitution on aromatic ring subsequentely, the value of (IE) for this compound is less than both compounds (e) and (d). Because of both compounds (b) and (a) have withdrawing group (carboxylic and nitro group) substituted on aromatic ring, these inhibitors show less reactivity due to the presence of these group which let to minimise the electron density on aromatic ring, subsequently, let to decrease the inhibition efficiency.

Figure 3. The HOMO of the inhibitors.
4. Conclusion

We performed theoretical calculations of chromen azodyes derivative compounds as anti-corrosive for carbon steel based on density functional theory (DFT) with the Lee-Yang-Parr nonlocal correlation functional (B3LYP) method. The molecular structures have been optimized by using Gaussian 09 software with 6-311G basis set. These calculations are achieved to obtain a relation between the effect of electron characteristic and the inhibition activity. Quantum chemical calculations approve that the substitute of ortho group on the phenol ring by electron donor group lead to increase of the inhibition efficiency of the inhibitor. We concluded from the calculations the most controlling quantum parameters to influence the inhibition efficiency of antipyrine inhibitors are the energy gap $\Delta E$ and the softness $\sigma$. The inhibitor efficiency of azo dyes compounds according to these quantum parameters will be in the order: Inhibitor (e) > Inhibitor (d) > inhibitor (c) > inhibitor (b) > inhibitor (a).
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