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Experimental and Theoretical Study for Corrosion Inhibition in Normal Hydrochloric Acid Solution by Some New Phophonated Compounds

O. Senhaji [1], *R. Taouil* [1], *M. K. Skalli* [2], *M. Bouachrine* [3*], *B. Hammouti* [4], *M. Hamidi* [1],
S.S. Al-Deyab [5]

[1]Equipe de Chimie Physique Appliquée, U.M.I., Faculté des Sciences et Techniques, Errachidia, Maroc
[2]Laboratoire de Chimie Appliquée, U.S.M.B.A., Faculté des Sciences et Techniques, Fès, Maroc
[3]UMIM, Faculté Polydisciplinaire de Taza, Université Sidi Mohamed Ben Abdellah, Taza, Morocco.
[4]LACE-URAC18, Faculté des Sciences, Université Mohammed Premier, B.P. 717, 60000 Oujda, Morocco.
[5] Petrochemical Research Chair, Chemistry Department, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

[*]E-mail: bouachrine@gmail.com

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The synthesis of two derivatives (sodium methyldodecylphosphonate) A and (sodium methyl (11-methacryloyloxyundecyl) phosphonate) B was performed using the methods described by (Yactine et al. 2005; Senhaji et al. 2004). After purification, the compounds obtained are characterised. The inhibitory effect on the corrosion of the two derivatives A and B has been study using weight loss measurements. Results obtained show that the compound B is found the best inhibitor and its inhibition efficiency (E %) reached up to 90% for 5 x 10^{-4} M of B. On the other hand and in order to determine the relationship between the molecular structure of these compounds and inhibition efficiency, quantum chemical parameters such as the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), the fraction of electrons transferred (ΔN), and the total energy (TE), were calculated. The theoretically obtained results were found to be consistent with the experimental data reported.

Keywords: Synthesis, pyridine, Hydrochloric acid, Phosphonate, Adsorption, DFT calculations

1. INTRODUCTION

Corrosion is an electrochemical process by which the metallic structures are destroyed gradually through anodic dissolution [1]. Combating corrosion in acidic environment can be achieved by addition of some specific compounds, called inhibitors [2]. Electronegative functional groups and л-electron in triple or conjugated double bonds as well as heteroatoms like sulphur, phosphorus, nitrogen and oxygen in their structure are the major adsorption centres. The modes of adsorption depend on (i) the chemical structure of the molecule, (ii) the chemical composition of the solution, (iii) the nature of the metal surface and (iv) the electrochemical potential of the metal-solution interface. The most important aspect of inhibition, normally considered by corrosion scientists is the relation between the molecular structure and corrosion inhibition efficiency [3-5].

On the other hand, ionic liquids (ILs) are emerging as smart and excellent solvents, which are made of positive and negative ions that pack so poorly together that they are liquids near room temperature.[6-8] They offer significant properties such as negligible vapor pressure, high thermal stability, lack of inflammability, decent solubility for organic, inorganic and organometallic compounds, non-coordinating but good solvating ability, high ionic conductivity, and a wide electrochemical potential window [9-13]. Apart from these features each IL shows unique chemical and physical property by proper varying its cation and anion [14].

The concept of assessing the efficiency of an inhibitor of corrosion with the help of computational chemistry is to search for compounds with desired properties using chemical intuition and experience into a mathematically quantified and computerized form.

Once a correlation between the structure and activity or property is found, any number of compounds, including those not yet synthesized, can be readily screened employing computational methodology and a set of mathematical equations which are capable of representing accurately the chemical phenomenon under study [15-16].

The most efficient inhibitors are the organic compounds that have π bonds, heteroatoms (P, S, N, and O).

The inhibition effect mainly depends on some physicochemical and electronic properties of the organic inhibitor which relate to its functional groups, steric effects, electronic density of donor atoms, and orbital character of donating electrons, and soon [6,7]. The inhibiting mechanism is generally explained by the formation of a physically and/or chemically adsorbed film on the metal surface [8, 9]. Recently, theoretical explanations of the efficiency of corrosion inhibitors become very possible in parallel with the progress in computational hardware and the development of efficient algorithms [17-18].

Several quantum chemical methods and Quantum-chemistry calculations have been performed in order to study the molecular structure and the reaction mechanisms in order to interpret the experimental results as well as to solve chemical ambiguities and to correlate the inhibition efficiency to the molecular properties [19]. The structure and electronic parameters can be obtained by means of theoretical calculations using the computational methodologies of quantum chemistry. The geometry of the inhibitor in its ground state, as well as the nature of their molecular orbitals, HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) are involved in the properties of activity of inhibitors.

The relationships between the structural parameters and corrosion inhibition of those compounds have not been studied yet.

In the present paper, two derivatives P-containing compounds namely Sodium methyldodecylphosphonate A and sodium methyl (11-methacryloyloxyundecyl) phosphonate B were synthesized. The corrosion protection properties of these compounds the electrochemical behaviour of the mild steel 1M HCl was studied by gravimetric.

The more relevant molecular properties on its action as inhibition of the corrosion were calculated.

These properties are the highest occupied molecular orbital energy (E_{HOMO}), the lowest unoccupied molecular orbital energy (E_{LUMO}), energy gap (ΔE), dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I), the fraction of electrons transferred (ΔN), and the total energy (TE). The chemical structures of the studied derivatives are given in Figure 1.

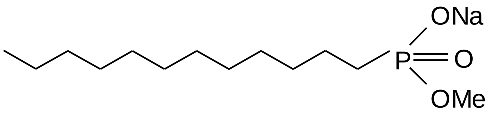
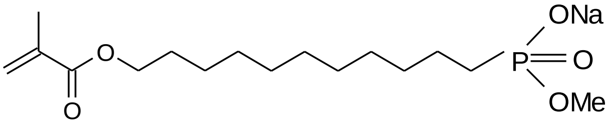
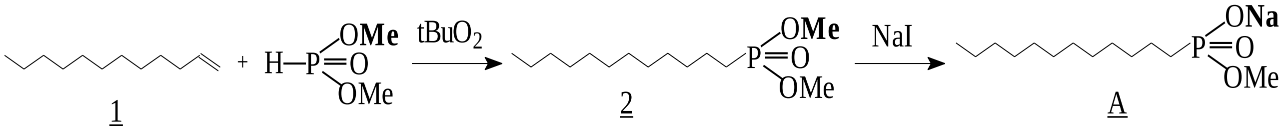
 sodium methyldodecylphosphonate	 sodium methyl (11-methacryloyloxyundecyl) phosphonate
A (M = 286 g.mol^{-1})	B (M = 356 g.mol^{-1})

Figure 1. The proposed structure of the studied compounds A & B

2. EXPERIMENTAL DETAILS

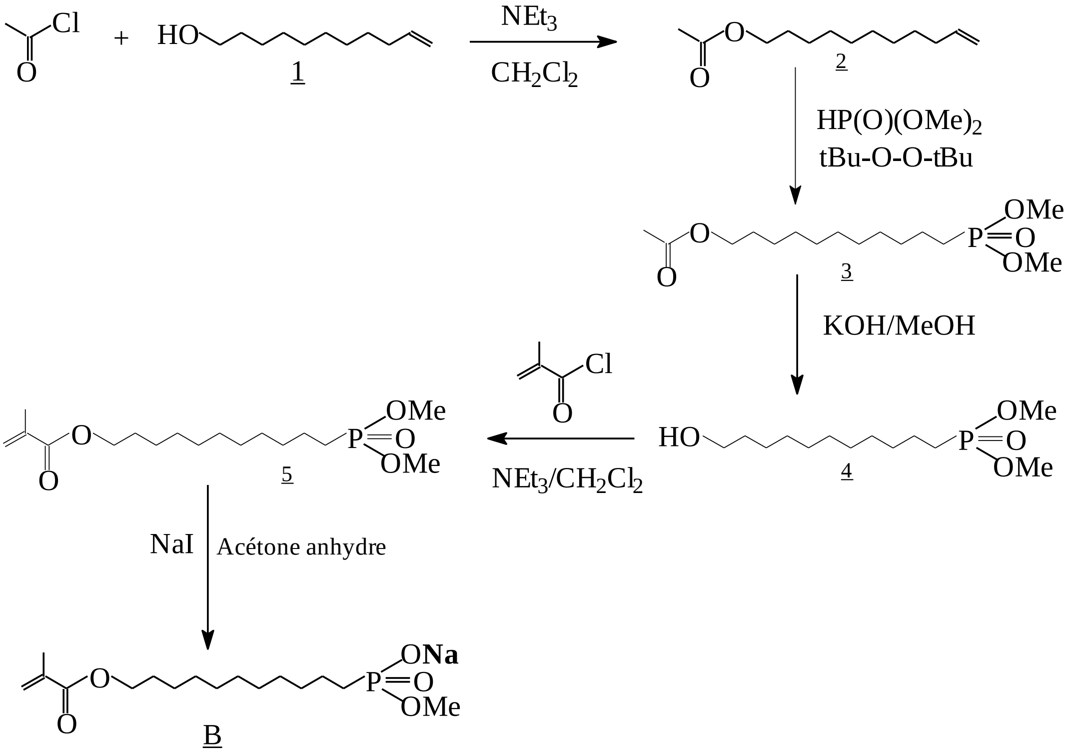
2.1. Synthesis

The surfactants A was synthesized according to method described by Yactine et al., [20] and summarized in scheme 1



Scheme 1. Synthesis of sodium methyldodecylphosphonate A

The surfactant B was synthesized according to method described by Senhaji et al., [21] and summarized in scheme 2



Scheme 2. Synthesis of sodium methyl (11-methacryloyloxyundecyl) phosphonate B

2.2. Weight loss measurements

Gravimetric measurements were carried out in a double-walled glass cell equipped with a thermostat-cooling condenser. The solution volume was 60 mL. The steel specimens used had a rectangular form (2.5 cm x 2 cm x 0.05 cm). The immersion time for the weight loss was 6 h at 308 K and 1 h at other temperatures. After the corrosion test, the specimens of steel were carefully washed in double-distilled water, dried, and then weighed. The rinse removed loose segments of the film of the corroded samples. Triplicate experiments were performed in each case and the mean value of the weight loss is reported. Weight loss allowed us to calculate the mean corrosion rate as expressed in mg.cm^{-2} h^{-1}.

2.3. Computational details

DFT (density functional theory) methods were used in this study. These methods have become very popular in recent years because they can reach exactitude similar to other methods in less time and less expensive from the computational point of view. In agreement with the DFT results, energy of the fundamental state of a polyelectronic system can be expressed through the total electronic density, and in fact, the use of electronic density instead of wave function for calculating the energy constitutes the fundamental base of DFT [22]. All calculations were done by GAUSSIAN 03 W software [23], using the B3LYP functional [24] and a 6-31G* basis set [25]. The B3LYP, a version of DFT method, uses Becke's three-parameter functional (B3) and includes a mixture of HF with DFT exchange terms associated with the gradient corrected correlation functional of Lee, Yang, and Parr (LYP). The geometry of all species under investigation was determined by optimizing all geometrical variables without any symmetry constraints. Frontier molecular orbitals (*HOMO* and *LUMO*) may be used to predict the adsorption centers of the inhibitor molecule. For the simplest transfer of electrons, adsorption should occur at the part of the molecule where the softness, σ , which is a local property, has the highest value. According to Koopman's theorem [26], the energies of the *HOMO* and the *LUMO* orbitals of the inhibitor molecule are related to the ionization potential, *I*, and the electron affinity, *A*, respectively, by the following relations: $I = -E_{HOMO}$ and $A = -E_{LUMO}$. Absolute electronegativity, χ , and absolute hardness, η , of the inhibitor molecule are given by [27]. $\chi = \frac{I + A}{2}$ and $\eta = \frac{I - A}{2}$. The softness is the inverse of the hardness: $\sigma = \frac{1}{\eta}$.

3. RESULTS AND DISCUSSION

3.1. Characterizations

The ^{1}H and ^{31}P NMR spectra have been registered at room temperature with a BrukerAC200 instrument using $CDCl_3$ as a solvent. The references for ^{1}H and ^{31}P NMR have been the tetramethylsilane (TMS) and orthophosphoric acid (H_3PO_4). Conductivity has been measured at 25 8C with a conductometer PHM 210 MeterLab. Radiometer.

The ^{1}H and ^{31}P NMR spectra (D_2O) confirm the structure of surfactant A [20].

The ^{1}H NMR (Figure 2) confirms the structure of the expected monosalt B [21]. Indeed, the integration of the signal of methacrylic ester at 3,5 ppm shows that monodealkylation has taken place.

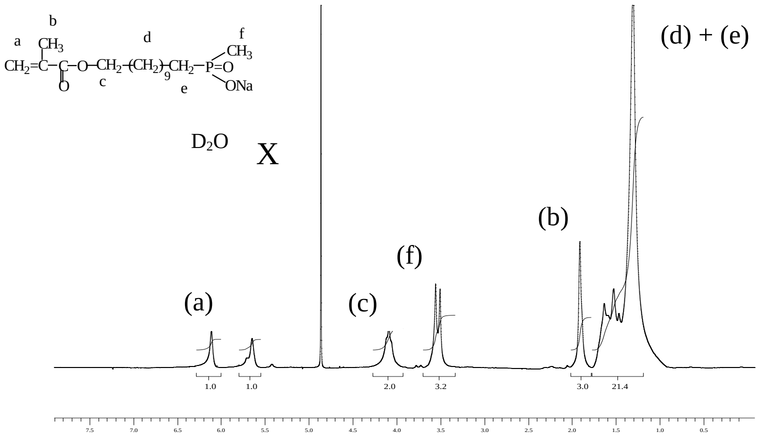


Figure 2. ^{1}H NMR spectrum (D_2O) of the synthesized surfactant B.

On the other hand the ^{31}P NMR in D_2O (Figure 3) reveals a peak at 29,98 ppm which signifies that phosphonic acid salt has been formed :

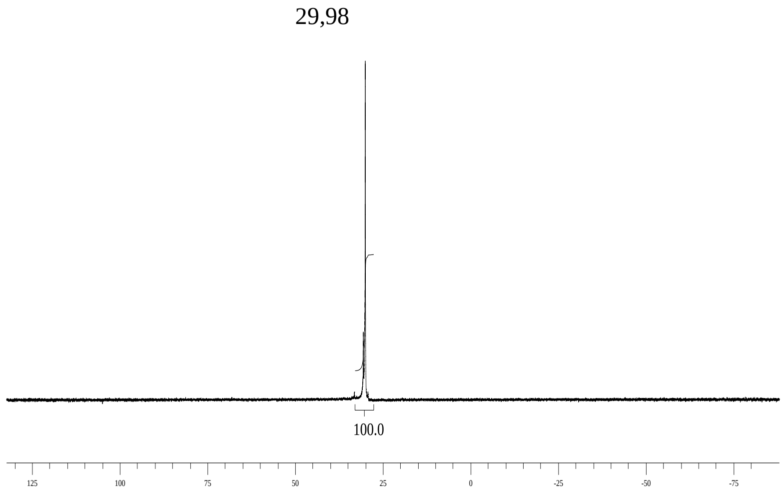


Figure 3. ^{31}P NMR spectrum (D_2O) of Surfactant B

3.2. Inhibitive effect of studied Compounds

Table 1. Gravimetric results of steel in acid without and with addition of A & B at 6h at 308K

Inhibitor	Concentration(M)	W(mg/cm^2.h)	Ew (%)	θ
Blank	1	1.15	-	-
	10^{-6}	1.042	9	0.09
	$5xl0^{-6}$	0.938	18	0.18
A	10^{-5}	0.774	33	0.33
	$5xl0^{-5}$	0.473	59	0.59
	10^{-4}	0.265	77	0.77
	$5xl0^{-4}$	0.194	83	0.83
	10^{-6}	0.987	14	0.14
	$5xl0^{-6}$	0.906	21	0.21
B	10^{-5}	0.655	43	0.43
	$5xl0^{-5}$	0.365	68	0.68
	10^{-4}	0.175	85	0.85
	$5xl0^{-4}$	0.118	90	0.90

Gravimetric measurements of steel were investigated in 1M HCl in the absence and presence of various concentrations of A and B at 6 h of immersion and at 308 K [22]. The inhibition efficiency (E_w %) was estimated by:

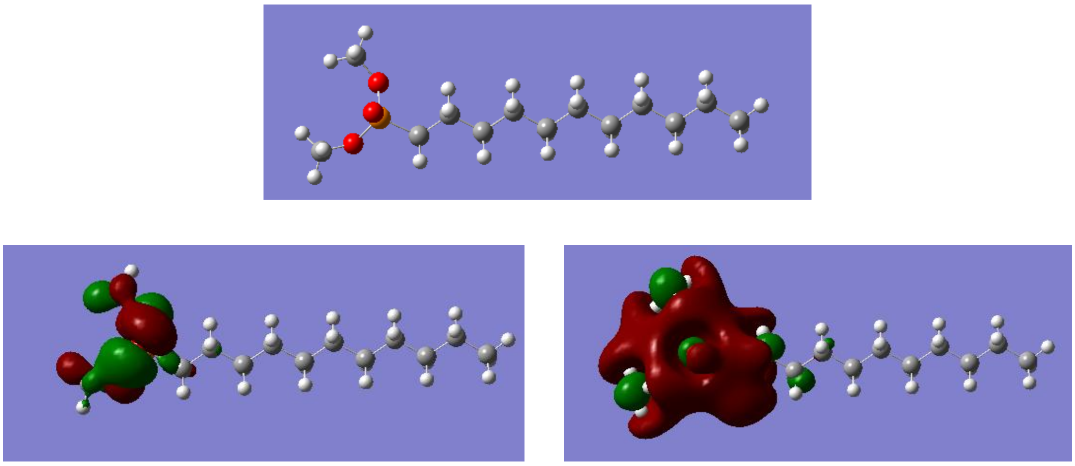
$$E_W\% = \left(1 - \frac{W_{corr}}{\overset{\circ}{W}_{corr}}\right) \times 100 \qquad (1)$$

where W_{corr} and $W_{corr\ (inh)}$ are the corrosion rates of steel in the absence and presence of the organic compound, respectively.

Table 1 collects the corrosion rates and the inhibition efficiencies evaluated from weight loss measurements for different inhibitor concentrations in 1M HCl.

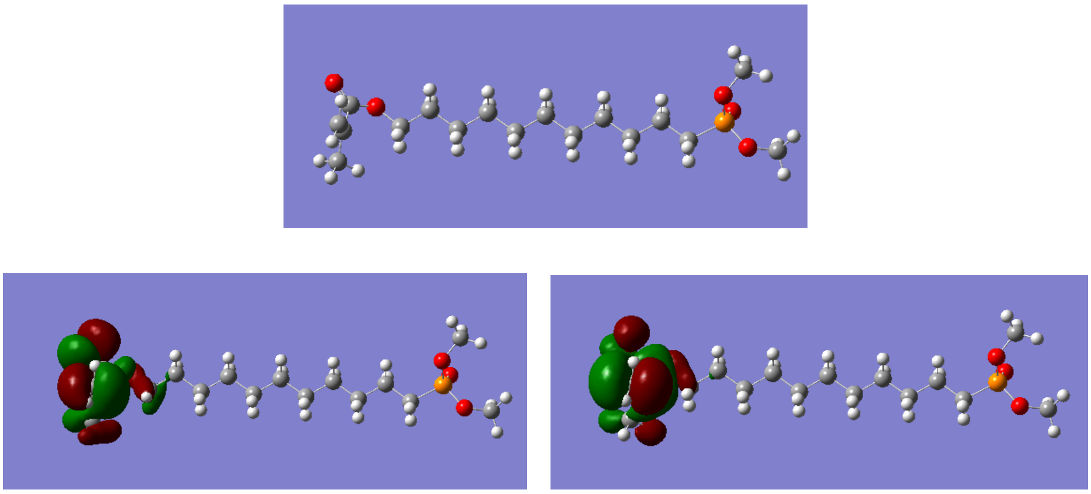
The corrosion rate decreases with the concentration of A and B and in turn the inhibition efficiency (E_w %) increases to attain 90% for 5.10^{-4}M B.

3.3. Theoretical results



HOMO LUMO

Molecule A



HOMO LUMO

Molecule B

Figure 2. The obtained molecular structures and *HOMO* and *LUMO* orbitals of the neutral inhibitor molecules A & B by *DFT/B3LYP/6-31G(d)*.

Quantum chemical calculations were performed to investigate the structural parameters affect the inhibition efficiency of inhibitors. Geometric and electronic structures of the inhibitors were calculated by the optimization of their bond lengths. The optimized molecular structures with minimum energies obtained from the DFT */B3LYP/6-31G(d)* calculations are given in Fig. 2.

Quantum chemical parameters are obtained from the calculations which are responsible for the inhibition efficiency of inhibitors such as the energies of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), energy gap (ΔE), dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I) and the total energy (TE) are collected in Table 2.

Table. 2. The calculated quantum chemical parameters of the studied molecules A & B

	A	B
E_{HOMO} (eV)	-6.827	-7.0626
E_{LUMO} (eV)	-0.48033	0.8356
ΔE gap (eV)	6.3467	7.8982
μ (debye)	5.4131	1.6388
E_w (%)	94	89
$I = -E_{HOMO}$ (eV)	6.827	7.0626
$A = -E_{LUMO}$ (eV)	0.48033	-0.8356
$\chi = \frac{I+A}{2}$ (eV)	3.6537	3.1135
$\eta = \frac{I-A}{2}$ (eV)	3.173	3.949
$\sigma = \frac{1}{\eta}$	0.31515	0.25322
TE (u.a.)	-1385.2115	-1079.9565

The energy of *HOMO* is often associated with the electron-donating ability of a molecule; high values of E_{HOMO} are likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy and empty molecular orbital. Therefore, the energy of *LUMO* indicates the ability of the molecule to accept electrons [28, 29]. So, the lower the value of E_{LUMO}, the more probable the molecule accepts electrons. The binding ability of the inhibitor to the metal surface increases with increasing of the HOMO energy values. So when we compared the studied compounds A and B, the calculations show that the compound A has the highest HOMO level at −6.827 eV and the lowest LUMO level at −0.48033 eV compared to the obtained parameters for compound B . This can explain that the highest inhibition efficiency of A is due to the increasing energy of the HOMO and the decreasing energy of the LUMO. This is in a good agreement with the experimental observations suggesting that the compound A has the highest inhibition efficiency (94%).

When we examine the obtained values of gap energies, the results obtained show that the compound A has a small $\Delta Egap$. This parameter provides a measure for the stability of the formed complex on the metal surface. The lower value of ΔE has, the higher stability is for the formed complex.

On the other hand, the most widely used quantity to describe the polarity is the dipole moment of the molecule [30]. Dipole moment is the measure of polarity of a polar covalent bond. It is defined as the product of charge on the atoms and the distance between the two bonded atoms. The total dipole moment, however, reflects only the global polarity of a molecule. For a complete molecule the total molecular dipole moment may be approximated as the vector sum of individual bond dipole moments. The theoretical study has shown that the dipole moment is well correlated with the inhibition efficiency when we compared the studied compounds A and B, the calculations show that the compound A has the highest value of dipole moment (5.4131 debye) compared to the obtained parameter for B (1,6388 debye). Indeed, the inhibition efficiency increases with increasing dipole moment.

The total energy of the best inhibitor A is equal to -1385.2115 u.a. This result indicated that the compound A is favourably adsorbed through the active centres of adsorption and especially the presence of two oxygen atoms in its structure.

Other quantum chemical parameters such as hardness (η) and softness (σ) were also calculated. Our theoretical results indicate that the compound A has a small hardness (η) and high softness (σ) compared to the obtained parameters obtained from the compound B. This is in a good agreement with the results reported in the literature (article egypte).

4. CONCLUSION

From the obtained results and by using the DFT calculations, the inhibition efficiency of the studied compounds s A and B is investigated that leads to the following conclusions:

- Using the B3LYP/6-31 G(d) method, the inhibition efficiency of the studied c compounds may be correlated to their molecular structure.
- The calculated dipole moments and Gap energy show reasonably good correlation with the efficiency of corrosion inhibition
- When we compared the two compounds A and B, the calculations show that the compound A has the highest HOMO level compared to obtained parameter for B. This can explain that the highest inhibition efficiency of A is due to the increasing energy of the HOMO. This is in a good agreement with the experimental observations suggesting that the compound A has the highest inhibition efficiency.

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