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Quantum Chemical Study of 2-Mercaptoimidazole, 2-Mercaptobenzimidazole, 2-Mercapto-5-Methylbenzimidazole and 2-Mercapto-5-Nitrobenzimidazole as Corrosion Inhibitors for Steel

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In order to analyze the influence of substituent groups, both electron-donating and electron-attracting and the number of π-electrons on the corrosion inhibiting properties of organic molecules, a theoretical quantum chemical study under *vacuo* and in the presence of water, using the Polarizable Continuum Model (PCM), was carried out for four different molecules, bearing similar chemical framework structure: 2-mercaptoimidazole (2MI), 2-mercaptobenzimidazole (2MBI), 2-mercapto-5-methylbenzimidazole (2M5MBI), and 2-mercapto-5-nitrobenzimidazole (2M5NBI). From an electrochemical study conducted previously in our group, (R. Álvarez-Bustamante, G. Negrón-Silva, M. Abreu-Quijano, H. Herrera-Hernández, M. Romero-Romo, A. Cuán, M. Palomar-Pardavé. *Electrochim. Acta*, 54, (2009) 539), it was found that the corrosion inhibition efficiency, IE, order followed by the molecules tested was 2MI > 2MBI > 2M5MBI > 2M5NBI. Thus 2MI turned out to be the best inhibitor. This fact strongly suggests that, contrary to a hitherto generally suggested notion, an efficient corrosion inhibiting molecule neither requires to be a large one, nor possesses an extensive π-electrons number. In this work, from a theoretical study a correlation was found between E_{HOMO}, hardness (η), electron charge transfer (ΔN), electrophilicity (W), back-donation ($\Delta E_{Back\text{-}donation}$) and the inhibition efficiency, IE. The negative values of E_{HOMO} and the estimated value of the Standard Free Gibbs energy for all the molecules (based on the calculated equilibrium constant) were negative, indicating that the complete chemical processes in which the inhibitors are involved, occur spontaneously.

Keywords: Steel; Corrosion inhibition; Quantum Chemistry; Sulphuric acid; 2-mercaptoimidazole; adsorption

1. INTRODUCTION

Recently, our research group has shown that both 2-mercaptobenzimidazole (2MBI) [1] and 2-mercaptoimidazole (2MI) [2] can be very useful corrosion inhibitors for steel under highly acidic conditions and pointed out that the effectiveness of the heterocyclic compound can be intimately associated to its molecular structure.

Many efforts have been done to try to understand which are the basic features that grant the corrosion inhibitory character to the organic compounds.

Theoretical studies at molecular level have been reported that aim at gaining insight on the molecules' chemical activity [3-7] and in particular to study corrosion inhibiting processes [8, 9] taking into account model molecules and their structural and electronic properties.

According to some quantum-chemical results, a relationship has been found between corrosion inhibition as the HOMO energy level increases [8-29], or as the HOMO-LUMO energy gap value decreases within a group of organic inhibitors [10, 12, 28, 30, 31].

Some authors [11, 13, 19, 22, 24, 27] found that the polarity of the organic compound affects the inhibitory character. Studies on chemical reactivity [6, 12-14, 17, 18] showed that the heteroatom from the molecules plays an important role within the inhibiting mechanism leading to a better understanding of this issue.

In this work, we studied four different small molecules which have similar chemical framework structure but with different substituent groups or heteroatoms: 2-mercaptoimidazole (2MI), 2-mercaptobenzoimidazole (2MBI) 2-mercapto-5-methylbenzimidazole (2M5MBI) and 2-mercapto-5-nitrobenzimidazole (2M5NBI), using electrochemical techniques [2] and theoretical quantum chemical calculations by applying the Density Functional Theory (DFT), in order to elucidate the inhibiting activity of these molecules through the knowledge of their structural and electronic properties.

2. PROCEDURE

2.1. Quantum-chemical calculations methodology

The calculations have been performed with *Gaussian03* [32] using the BeckeLYP functional [33, 34] and the 6-311+G(d,p) basis set for both cases: *in vacuo* and with the Polarizable Continuum Method (PCM) accounting for the solvent (water) effect [35, 36]. The PCM by Miertus et al. [35], SCRF methods (self-consistent reaction field) were used to perform calculations in solution. These methods model the solvent as a continuous with uniform dielectric constant (ε) and the solute is placed in a cavity within it.

The calculations accounted for the complete set of electrons and the geometry of all involved structures was fully optimized.

Computing was performed with a Pentium 4, 1.9 MHz and 500 Mb RAM workstation and molecules' visualization was carried out with Arguslab 4.0 commercial software [37-45] and the Gausview 2.02 software [32].

3. RESULTS AND DISCUSSION

3.1. Quantum-chemical background

The theoretical aspects of the inhibitor molecules performance have been studied to understand and describe the experimental observations [2] based on the structural and electronic properties of these inhibiting compounds.

To estimate the active sites pertaining to the different corrosion inhibitors considered in this work, see Figure 1, and their inhibiting features, a set of thermodynamic parameters [42-45] was devised from the Density Functional Theory [41], DFT, namely hardness (η), Fukui functions (f(r)) and chemical potential (μ).

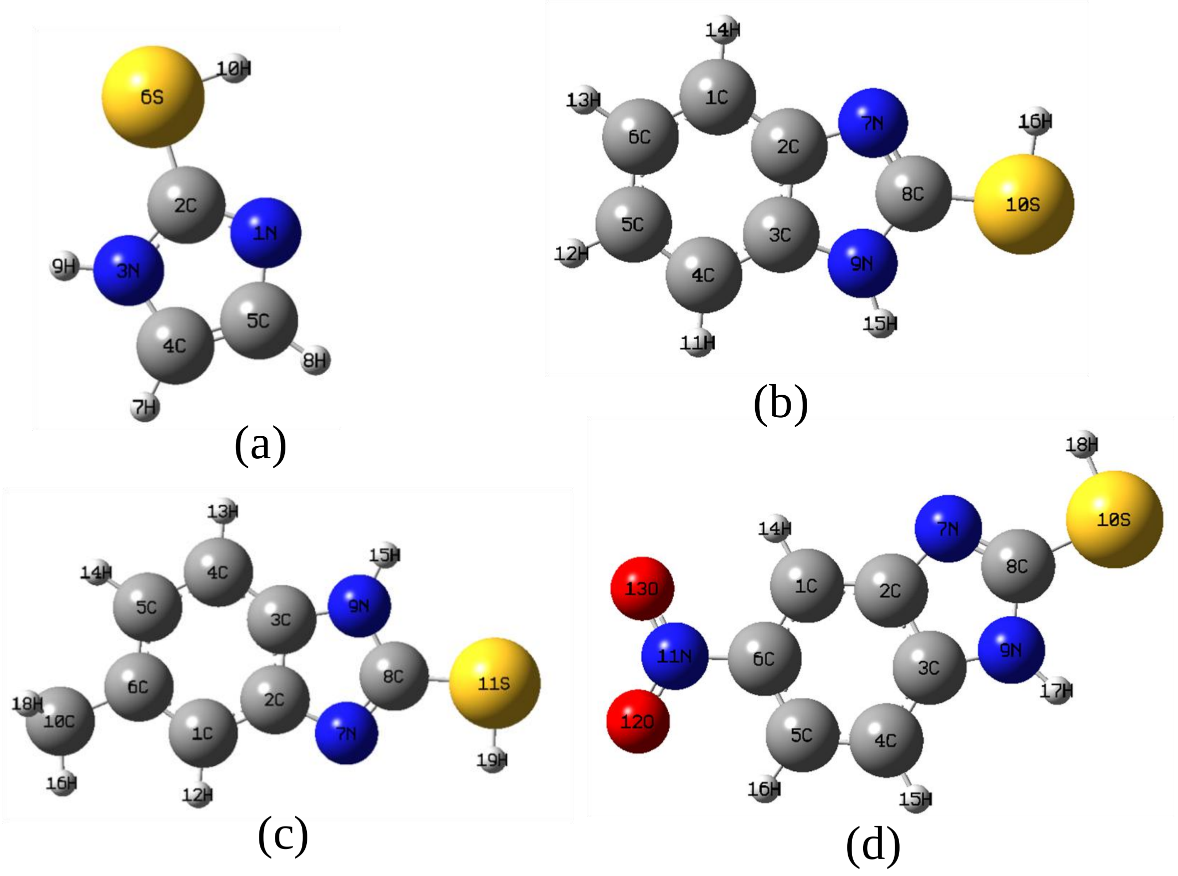


Figure 1. Optimized molecular structures: (a) 2-mercaptoimidazole (2MI), (b) 2-mercaptobenzoimidazole (2MBI), (c) 2-mercapto-5-methylbenzimidazole (2M5MBI) and (d) 2-mercapto-5-nitrobenzimidazole (2M5NBI).

The variables associated to DFT studies are the electronic density $(\rho(r))$ divided in spin contributions α and β, the systems' energy $\left(E\left[\rho^{\alpha}(r),\rho^{\beta}(r)\right]\right)$ and electron number (N), the multiplicity, the external potential (ν(r)) and the magnetic field associated to the media (B(r)) dependent on Bohr's magneton μ_b, which is useful to define spin conditions. From these quantities the following values can be found: the energy ($\varepsilon_i(r)$) of molecular orbitals' ($\phi_i(r)$). In order to evaluate the energy of the system, hence the electron density, the following functional expression was used:

$$E\left[\rho^{\alpha}(r),\rho^{\beta}(r)\right]=\sum_{i\sigma}\int d\mathbf{r}\,\phi_{i\sigma}^{*}(\mathbf{r})(-\tfrac{1}{2}\nabla^{2})\phi_{i\sigma}+J\left[\rho^{\alpha}(r)+\rho^{\beta}(r)\right]+E_{xc}\left[\rho^{\alpha}(r),\rho^{\beta}(r)\right] \\ +\int d\mathbf{r}\left[(v(\mathbf{r})+\mu_b B(\mathbf{r}))\,\rho^{\alpha}(\mathbf{r})+(v(\mathbf{r})-\mu_b B(\mathbf{r}))\,\rho^{\beta}(\mathbf{r})\right] \tag{1}$$

where J is the coulombic energy functional and E_{xc} is the exchange and correlation contribution which permits evaluation of the electron interaction in the system, considering the interactions amongst three or more bodies.

The differentiation process applied to the energy with a set of variables of the system, will produce different thermodynamic response coefficients useful to predict a progress in a chemical reaction. [42, 45, 46]

Particular attention is given to the response coefficients obtained after first differentiation, which are associated to the chemical potential, μ_N, and the spin potential, μ_s:

$$-\chi=\mu_N=\left(\frac{\partial E(r)}{\partial N}\right)_{N_s} \qquad \mu_s=\left(\frac{\partial E(r)}{\partial N_s}\right)_{N} \tag{2}$$

where χ is the electronegativity of the molecule. The chemical potential can also be evaluated in terms of the frontier orbital energies:

$$\mu_N=\tfrac{1}{2}\left[E_{HOMO}+E_{LUMO}\right] \tag{3}$$

From the second differentiation is possible to obtain the response coefficients associated to the hardness:

$$\eta_{NN}=\left(\frac{\delta\mu_N}{\delta N}\right)_{N_s,v,\mathbf{B}}=\left(\frac{\delta^2 E(r)}{\delta N^2}\right)_{N_s,v,\mathbf{B}}\approx\tfrac{1}{2}\left(E_{HOMO}-E_{LUMO}\right) \tag{4}$$

Moreover, the directional components for a molecule (M) that accepts charge:

$$\eta_{NN}^{-}=\left(\frac{\delta\mu_N}{\delta N}\right)_{N_s}\cong\frac{\left(\mu_N^{M}-\mu_N^{M(cation)}-\mu_N\right)}{\Delta N} \qquad \eta_{NN}^{+}=\left(\frac{\delta\mu_N}{\delta N}\right)_{N_s}\cong\frac{\left(\mu_N^{M(anion)}-\mu_N^{M}\right)}{\Delta N} \tag{5}$$

In a similar way electrophilicity index (W) can be obtained from the definitions of global hardness and chemical potential as follows:

$$W=\frac{\mu_N^{2}}{2\eta_{NN}} \tag{6}$$

Furthermore, the following derivation process helps to obtain another important thermodynamic response coefficient, the Fukui function:

$$f(\mathbf{r})=\left(\frac{\delta\mu_N}{\delta v(\mathbf{r})}\right)_N=\left(\frac{\delta\rho(\mathbf{r})}{\delta N}\right)_v \tag{7}$$

Also, the generalized Fukui functions [42-46]:

$$f_{NN}(\mathbf{r})=\left(\frac{\delta\mu_N}{\delta v(\mathbf{r})}\right)_{N,N_s}=\left(\frac{\delta\rho(\mathbf{r})}{\delta N}\right)_{N_s,v} \qquad f_{sN}(\mathbf{r})=-\frac{1}{\mu_B}\left(\frac{\delta\mu_N}{\delta\mathbf{B}(\mathbf{r})}\right)_{N,N_s}=\left(\frac{\delta\rho_s(\mathbf{r})}{\delta N}\right)_{N_s,v}$$

$$f_{Ns}(\mathbf{r})=\left(\frac{\delta\mu_s}{\delta v(\mathbf{r})}\right)_{N,N_s}=\left(\frac{\delta\rho(\mathbf{r})}{\delta N_s}\right)_{N,v} \qquad f_{ss}(\mathbf{r})=-\frac{1}{\mu_B}\left(\frac{\delta\mu_s}{\delta\mathbf{B}(\mathbf{r})}\right)_{N,N_s}=\left(\frac{\delta\rho_s(\mathbf{r})}{\delta N_s}\right)_{N,v} \tag{8}$$

The analysis of the Fukui functions associated to a molecule is useful to obtain a term associated with the ability of a system to modify its charge and/or multiplicity. To describe these phenomena, the Fukui functions that best represent the system are:

$$f_{Ns}^{-}(r)\cong\frac{\left(\rho_M(r)-\rho_{M(cation)}(r)\right)}{\Delta N_s} \qquad f_{Ns}^{+}(r)\cong\frac{\left(\rho_{M(anion)}(r)-\rho_M(r)\right)}{\Delta N_s} \tag{9}$$

In this work's case, both spin and charge changes were considered, through the following approximations, because at the electrodes' surface the changes of the electrical potential can reflect charge changes associated to formation of anionic or cationic species. This also can be approximated through the following expressions:

$$f_{Ns}^{-}(r)\cong\tfrac{1}{2}\left[\left(\phi_{HOMO}(r)\right)^2-\left(\phi_{LUMO}(r)\right)^2\right] \qquad f_{Ns}+(r)\cong\tfrac{1}{2}\left[\left(\phi_{LUMO}(r)\right)^2-\left(\phi_{HOMO}(r)\right)^2\right] \tag{10}$$

A global parameter of the molecule such as the hardness (eq. 4) and a local description of the molecule like the Fukui function (eq. 9 or eq. 10), were used to analyze the electron transfer processes [42-50] to evaluate the sites where the molecule will receive charge (f^{+}(r)) when engaged by a nucleophilic reagent or the preferred sites to donate charge (f^{-}(r)) when engaged by an electrophilic reagent. There are more detailed studies that can be used to determine the effect of a specific functional group in a molecule [43, 47] or to make a most specific atomic analysis. From these studies the condensed Fukui´s functions, also called Fukui´s indexes, were derived. To calculate such functions is necessary to adopt a partition scheme of the electronic density among all the atoms of the molecule, to associate a charge to each of them. In this situation, the electron density around an atom is associated with its net charge. If Z_i is the nuclear charge of the *i*-th atom, and $\rho_N^i(r)$ is the electron density around it, then the net charge of the *i*-th atom of the molecule (M) is given by $q_N^i=Z_i-\int dr\,\rho_N^i(r)$ and finally the Fukui´s indexes are defined as [48-51]:

$$f_{ss}^{-} \cong q_M^i - q_{M(cation)}^i \qquad\qquad f_{ss}^{+} \cong q_{M(anion)}^i - q_M^i \qquad (11)$$

For the sake of notation simplicity, the set of thermodynamic parameters employed in this work were defined as, η for the hardness (eq. 4), $f(r)$ for the Fukui function (eq. 10), and f_i, for the Fukui indexes (eq.11).

To estimate the hardness, the Fukui function and the Fukui´s indexes, it was important to consider that the simulation process to evaluate the electron density must describe adequately the system [7, 52]. Due to this fact, a Hartree-Fock-type density is meaningful, but including a correlation-type density [29, 53].

3.2. Theoretical assessment

The results of the geometries' optimization of the selected compounds are presented in Figure 1. The frameworks of these geometries show planar configurations for all the inhibitors.

Quantum-chemical indexes like E_{HOMO}, E_{LUMO}, ΔE ($|E_{HOMO} - E_{LUMO}|$) or hardness η, and dipole moment are summarized in Table 1. To analyze the theoretical results obtained, it is necessary to bear in mind that the trend for the experimental inhibitor's efficiency was 2MI > 2MBI > 2M5MBI > 2M5NBI**.** It is known that E_{HOMO} is often related to electron donation ability of the inhibitor molecules toward the metallic surface atoms, and it is expected that a higher E_{HOMO} value would favor a greater charge transfer [7, 10-14, 29, 54, 55].

Table 1. Values for E_{HOMO}, E_{LUMO} $|E_{HOMO} - E_{LUMO}|$(GAP), global hardness (η) dipole moment for the inhibitors (in vacuo/with solvent) and total energy stabilization by solvent effect (ΔE_{solv}).

Inhibitor	E_{HOMO} /eV	E_{LUMO} /eV	GAP /eV	η /eV	Dipole /eV	ΔEsolv /eV
2MI	-5.09/-5.02	-1.16/-0.69	3.93/4.33	1.97/2.17	2.66/3.90	-0.72
2MBI	-5.25/-5.21	-1.40/-1.38	3.86/3.82	1.93/1.91	2.40/3.86	-0.80
2M5MBI	-5.13/-5.11	-1.32/-1.33	3.81/3.78	1.91/1.89	2.22/3.65	-0.78
2M5NBI	-5.92/-5.61	-3.28/-3.55	2.64/2.07	1.32/1.04	7.44/11.61	-1.15

According to our results, the values of E_{HOMO} show the following behavior 2MI > 2M5MBI > 2MBI > 2M5NBI for this property. In this case, the largest E_{HOMO} corresponds to 2MI (see Table 1) in line with the aforementioned experiments and the lowest E_{HOMO} corresponds to 2M5NBI that in terms of activity is the worst inhibitor. Some authors [50-55] have found that a smaller value of the hardness is related to greater stability of the surface-inhibitor complex formed. Moreover, smaller values of E_{LUMO} show better capacity of the inhibitor to accept electrons. The trend obtained for the E_{LUMO} values was 2M5NBI < 2MBI < 2M5MBI < 2MI and for the hardness was 2MI > 2MBI > 2M5MBI > 2M5NBI, as it can be observed in Table 1. Some authors have reported a relationship between these properties while others claim there is not such a relationship [54, 55]. Our results indicate no relationship between these properties, the hardness and E_{LUMO} agrees with later works. It seems that the larger the hardness value the greater the inhibitor efficiency, which is in agreement with our experimental results [2]. On the other hand, while some previous papers showed that the E_{LUMO} value is over the Fermi level [31, 56-62], the computational results for the currently studied molecules show that the E_{LUMO} value has a negative value, thus indicating the capability to accept electrons too.

The theoretical parameters were calculated *in vacuo* while the electrochemical corrosion phenomena occur in an aqueous phase. For this reason, the Polarizable Continuum Method (PCM) was employed in order to consider the solvent effect (water) in the calculations. Table 2 also shows the results when water is taken into account. The results indicate that the larger the total stabilization energy the greater the increase in the dipole moment obtained. Solvent effect provides stabilization to the molecules, vide ΔE_{solv} in Table 1. Also, the E_{HOMO} values with solvent effect are greater than *in vacuo* conditions for all the inhibitors and there is not a proportional effect for the E_{LUMO} values for the solvent effect systems. Considering the solvent, the E_{LUMO} value drops for the case of 2M5NBI from -3.28 to -3.55, while the E_{LUMO} value jumped for the 2MI from -1.16 to -0.69 while for the 2MBI and 2M5MBI it remained almost constant. The hardness for 2MI is wider when the solvent effect is taken into account than *in vacuo* conditions, for the rest of the inhibitors there are no significant differences, but the hardness always decrease by solvent effect. In spite of the differences, the same trend was observed for both approximations.

The results from calculations of hardness and chemical potential *in vacuo* as well as with the solvent (water) effect are summarized in Table 2, which reveal that the 2MI exhibits the largest overall hardness values in both phases, with and without solvent effect. Note that the said hardness increases for the 2MI due to the solvent effect, while for the rest of the inhibitors it decreases in the presence of water. However, the chemical potential and the electronegativity decreased in solution in all cases, with the 2MI being the less electronegative. For the overall electrophilicity and according to the computed values (see Table 2), the 2MI exhibited a better nucleophilic character, while the 2M5NBI was lower than the rest. It is well known that cations have electrophilic character, therefore a better interaction of 2MI, 2MBI and 2M5MBI with the metallic surface would be expected than for 2M5NBI, see Table 2.

Table 2. Global reactivity descriptors for inhibitors 2MI, 2MBI, 2M5MBI and 2M5NBI in eV, the values reported are for in vacuo conditions and with solvent effect.

Inhibitor	Chemical Potential (μ) /eV		Global Hardness (η) /eV		Electrophilicity (W) /eV	
	in vacuo	solv. Effect	in vacuo	solv. Effect	in vacuo	solv. effect
2MI	-3.13	-2.86	1.96	2.16	2.49	1.89
2MBI	-3.32	-3.29	1.93	1.91	2.87	2.84
2M5MBI	-3.22	-3.22	1.90	1.89	2.73	2.74
2M5NBI	-4.60	-4.58	1.32	1.03	8.01	10.14

Based on the Pearson theory [14, 24, 25, 59] the fraction of electrons transferred (ΔN) from the inhibitor molecule to the metallic atom can be calculated. Since a metallic surface and an inhibitor molecule have different electronegativity, the theoretical reported value [14, 24, 59] for bulk iron χ_{Fe} is about 7eV, and the overall hardness $\eta_{Fe} = 0$, assuming that the metallic bulk I = A [50, 59], due to the characteristics of the neutral metallic atoms; where I is the ionization potential and A the electron affinity. The electronegativity of the inhibitor molecules is lower than the bulk iron: hence, electrons move from the molecules with lower electronegativity (inhibitor compound) toward that of a higher value (metal surface) until the equilibrium in chemical potentials is reached. The calculation of ΔN is obtained from the following formula:

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \tag{12}$$

The experimental inhibition efficiency and the theoretical value of the fractions transferred under both conditions, *in vacuo* and in the presence of water are presented in Table 3. The values of ΔN indicate the trend within a set of molecules and the highest value of ΔN is related to high inhibitor efficiency. However, a clearer understanding of this parameter is not yet available. Even more, our results indicate an opposite behavior when the solvent is accounted for, since the higher ΔN corresponds to 2M5NBI which is the less effective inhibitor and the lower ΔN value corresponds to 2MI which is the best one. The trend in ΔN in the presence of water follows 2M5NBI > 2M5MBI > 2MBI > 2MI while *in vacuo* conditions this is not completely clear.

Table 3. Theoretical transferred electron fraction (ΔN) and Back-donation (eV) calculated for both in vacuo and with solvent effect.

Inhibitor Molecules (20 ppm)	Transferred electrons fraction		Back-donation /eV	
	in vacuo	solv. Effect	in vacuo	solv. Effect
2MI	0.99	0.96	-0.591	-0.639
2MBI	0.95	0.97	-0.480	-0.477
2M5MBI	0.99	1.00	-0.482	-0.478
2M5NBI	0.91	1.17	-0.476	-0.472

According to Gómez et al. [8], 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 [8]:

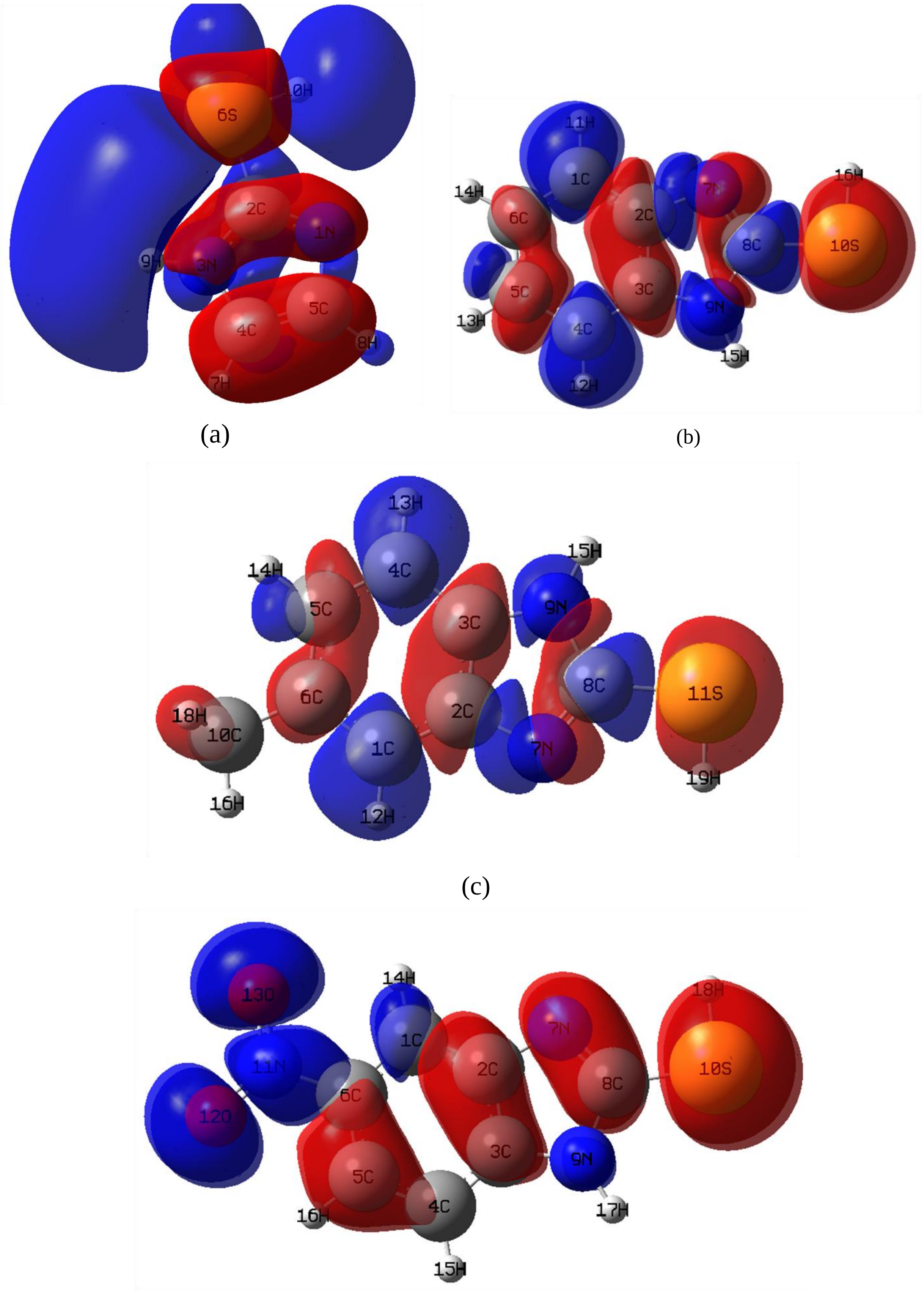
$$\Delta E_{Back-donation} = -\frac{\eta}{4} \qquad (13)$$

The $\Delta E_{Back\text{-}donation}$ implies that when $\eta > 0$ and $\Delta E_{Back\text{-}donation} < 0$ 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 increase as the hardness increases. In Table 3, the calculated $\Delta E_{Back\text{-}donation}$ values for both, *in vacuo* condition and with solvent effect are included. The order followed is: 2MI > 2MBI > 2M5MBI > 2M5NBI, which indicates that back-donation is favored for the 2MI, which is the best inhibitor. Finally, an analysis of the charges under the Mulliken scheme was done to assess changes on the 2MI by addition of substituent groups, especially over the sulphur atom and the carbon atom (6C) bonded to the substituent group for the 2M5MBI and 2M5NBI compounds.

The atomic NBO charges for the most important centers *in vacuo* and with solvent effect, are summarized in Table 4. Redistribution of the NBO charge is obtained by the presence of a substituent; the most favorable sites for the interaction with the metal surface were the following atoms: 11S, 3C and 7N for 2MI; 11S, 1C, 4C, 5C and 7N for 2MBI; 11S, 1C, 4C, 5C and 7N for 2M5MBI; and 11S, 4C and 7N for 2M5NBI affected atoms are the 2C, 4C, 5C, 6C, 8C and 11S, because these atoms have a larger negative charge, which suggests that those active centers with excess charges could act as a nucleophilic group. As it has been expected, the methyl and nitro group substitution in the 2MBI molecule, modified the charge distribution of the 2MBI framework, for which when a methyl group is in the structure the carbons 6C and 2C, are the most affected, while for the nitro group substitution is the carbon 6C. Generally, its behavior is more clear as a electroattractor group than for the methyl group as electrodonator, as can be seen in the Table 4.

Table 4. Representative atomic NBO charges for the different inhibitors compounds. See the Figure 1 for the atomic levels.

Inhib	**2MI**			**2MBI**			**2M5MBI**			**2M5NBI**		
	q	qsolv	f_i^-	q	qsolv	f_i^-	q	qsolv	f_i^-	q	qsolv	f_i^-
7N	-0.515	-0.583	-0.031	-0.513	-0.578	-0.024	-0.514	-0.579	-0.022	-0.500	-0.555	-0.027
8C	0.216	0.210	-0.017	0.246	0.247	-0.004	0.245	0.246	-0.004	0.250	0.255	-0.002
9N	-0.552	-0.551	-0.053	-0.562	-0.558	-0.033	-0.562	-0.558	-0.029	-0.556	-0.543	-0.042
1C	---	---	---	-0.198	-0.225	-0.015	-0.200	-0.227	-0.011	-0.180	-0.190	-0.015
2C	-0.066	-0.097	-0.017	0.102	0.114	-0.001	0.120	0.109	-0.001	0.119	0.115	0.000
3C	-0.092	-0.092	-0.023	0.122	0.119	-0.003	0.117	0.113	-0.001	0.145	0.164	0.005
4C	-0.066	-0.097	-0.017	-0.237	-0.242	-0.006	-0.229	-0.234	-0.003	-0.225	-0.220	-0.003
5C	---	---	---	-0.206	-0.226	-0.022	-0.202	-0.220	-0.016	-0.194	-0.197	-0.017
11S	-0.006	0.025	-0.076	0.044	-0.558	-0.076	0.042	0.011	-0.071	0.065	0.044	-0.077
15H	0.462	0.407	-0.343	0.409	0.465	-0.316	0.409	0.465	-0.319	0.217	0.247	-0.117
19H	0.162	0.204	-0.132	0.164	0.217	-0.165	0.163	0.216	-0.145	0.223	0.168	-0.198
6C	---	---	---	-0.217	-0.226	-0.021	-0.045	-0.050	-0.015	0.068	0.064	-0.020



(a) (b)

(c)

(d)

Figure 2. Isosurfaces of the Fukui function distribution for the different inhibitors conditions. The isosurface value is 0.02.

In Figure 2, a schematic representation of the Fukui functions obtained from the eq. 10 is showed. The isosurface representation is for $f^{-}_{Ns}(r)$, but for the case of $f^{+}_{Ns}(r)$, the representation is very similar, as the can be noticed in eq. 10. The difference between these functions is only the sign, which turn out to be positive or negative according to the function. Under this scheme, the result suggests that this group of molecules has the ability to act as charge donor or acceptor, since the Fukui functions, $f^{-}_{Ns}(r)$ and $f^{+}_{Ns}(r)$, have a high contribution over the complete molecule, then a dual behavior could be expected that agrees too with the back-donation found; both results are in line with the experimental observation [2], since the 2MI proved to be a mixed-type inhibitor, as it affected both anodic and cathodic process. In fact, if the isosurfaces of the group of inhibitors are compared, Figure 2, then 2MI has an important contribution in the region over the sulphur atom than the rest of the inhibitors. This result suggests that maybe the interaction with the metallic surface is through this atom mainly. Although the rest could contribute to the interaction too; even though the hardness is the greatest for the 2MI than for the rest, but the E_{LUMO} value has a negative value, which means certain capability to accept electrons.

It is important to stress out that Ivanova and Pindeva [63] using solid-state linear dichroic infrared (IR-LD) spectral analysis and *ab initio* calculations have shown that the protonation of benzimidazoles and 1,2,3-benzotriazoles can be occurring under acidic conditions. Thus it will very important to determine experimentally the acidity constant of each of the molecules considered here in order to carry out the theoretical analysis, in its case, the appropriate protonated or unprotonated molecules: this study is currently being carried out in our laboratory.

4. CONCLUSIONS

As previously shown experimentally (R. Álvarez-Bustamante, G. Negrón-Silva, M. Abreu-Quijano, H. Herrera-Hernández, M. Romero-Romo, A. Cuán, M. Palomar-Pardavé. *Electrochim. Acta*, 54, (2009) 539) the IE order for the molecules tested was 2MI > 2MBI > 2M5MBI > 2M5NBI. 2MI showed the best corrosion efficiency as inhibitor in spite of the lack of multiple bonds, π-electrons conjugated and polar part. The 2MI compound reached a relative maximum inhibiting efficiency of 98.5 % at 25 ppm concentration, following the Langmuir isotherm with an adsorption standard Gibbs Free Energy difference (ΔG^{0}_{ads}) of -26.8 kJ mol^{-1}. The 2MI IE was measured as a function of time, where the IE decreases linearly with time displaying a slope of -0.03h^{-1}, after 800 evaluation hrs. After this time, the 2MI IE falls to 70 % and it remains constant up to 1200 hrs. It is shown that this compound can affect both the anodic and cathodic processes, thus it can be classified as a mixed-type inhibitor. The values obtained for the standard Gibbs free energies of adsorption and the negative values of E_{HOMO} corroborates that physical adsorption of the inhibitors tested is effective onto the metal surface.

In this work it was found a quantitative relationship between E_{HOMO}, hardness (η), electron charge transfer (ΔN), Electrophilicity (W)**,** Back-donation ($\Delta E_{Back\text{-}donation}$) and the inhibition efficiency for the tested compounds. All these parameters represent better the actual experimental situation. As comparing the 2MI with the other inhibitors, it exhibits a better nucleophilic character; the highest

E_{HOMO} and the highest electron charge transfer (ΔN), hence underlining its good ability as an electro-donator. It too has the largest hardness and therefore a favorable back-donation charge. These results were found for both phases, namely with and without solvent effect.

According to the Fukui functions analysis, a dual behavior could be expected, since the contributions of both $f^{-}_{Ns}(r)$ and $f^{+}_{Ns}(r)$, have a large contribution over the complete molecule being largest for the 2MI with an important contribution in the region over the sulphur atom than the rest of the inhibitors, thus suggesting that the interaction with the metallic surface could be through this atom mainly.

The substituting groups as electrondonors or electroattractors do not have an important influence on the behavior over the 2MBI inhibitor, because from the experimental and theoretical point of view, the 2MBI is better inhibitor than the 2M5MBI or 2M5NBI, no matter the substituent's character.

Although a number of satisfactory quantum chemical parameters showed a good correlation with the inhibition efficiency of various inhibitors, there is still a lack of a simple correlation between some others like dipole and E_{LUMO} with the inhibition efficiencies.

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References

1. P. Morales-Gil, G. Negrón-Silva, M. Romero-Romo, C. Ángeles-Chávez, M. Palomar-Pardavé, *Electrochim. Acta* 49, (2004) 4733.
2. R. Álvarez-Bustamante, G. Negrón-Silva, M. Abreu-Quijano, H. Herrera-Hernández, M. Romero-Romo, A. Cuán, M. Palomar-Pardavé. *Electrochim. Acta,* 54, (2009) 539.
3. S. Corona-Avendaño, G. Alarcón-Ángeles, G.A. Rosquete-Pina, A. Rojas-Hernández, A. Gutiérrez, M.T. Ramírez-Silva, M. Romero-Romo, M. Palomar-Pardavé, *J. Phys. Chem. B,* 111 (2007) 1640.
4. L.H. Mendoza-Huizar, M. Palomar-Pardavé, J. Robles, *Electrochim. Acta* (2001) 2749.
5. J.A. Cobos-Murcia, L. Galicia, A. Rojas-Hernández, M.T. Ramírez-Silva, R. Álvarez-Bustamante, M. Romero-Romo, G. Rosquete-Pina, M. Palomar-Pardavé, *Polymer* 46 (2005) 9053.
6. Y. Yan,W. Li, L. Cai, B. Hou, *Electrochim. Acta* 53 (2008) 5953.
7. K.F. Khaled, *Electrochim. Acta* 53 (2008) 3484.
8. B. Gómez, N. V. Likhanova, M. A. Domínguez-Aguilar, R. Martínez-Palou, A. Vela, and J. L. Gázquez, *J. Phys. Chem. B* 110 (2006) 8928.
9. O. Olivares, N.V. Likhanova, B. Gómez, J. Navarrete, M. E. Llanos-Serrano, E. Arce, J. M. Hallen, *Appl. Surf. Sci.* 252 (2006) 2894.
10. P. Bothi, M. Gopalakrishnan, *Mater. Lett.* 62 (2008) 113.
11. Y.S. Li, A. Ba, M.S. Mahmood, *Electrochim. Acta* 53 (2008) 7859.

12. P.C. Okafor, M.E. Ikpi, I.E. Uwah, E.E. Ebenso, U.J. Ekpe, S.A. Umoren, *Corros. Sci.* 50 (2008) 2310.
13. P. de Lima-Neto, A.P. de Aráujo, W.S. Aráujo, A.N. Correia, *Prog. Org. Coat*. 62 (2008) 344.
14. L.R. Chauhan, G. Gunasekaran, *Corros. Sci.* 49 (2007) 114.
15. T. Fallavena, M. Antonow, R.S. Goncalves, *Appl. Surf. Sci.* 253 (2006) 566.
16. M.I. Awad, J. Appl. Electrochem. 36 (2006) 1163.
17. M. Zubielewicz, W. Gnot, *Prog. Org. Coat.* 49 (2004) 358.
18. G. Gunasekaran, L.R. Chauhan, *Electrochim. Acta* 49 (2004) 4387.
19. E. Stupnisek-Lisac, A. Gazivoda, M. Madzarac, *Electrochim. Acta* 47 (2002) 4189.
20. A.V. Shanbhag, T.V. Venkatesha, R.A. Prabhu, R.G. Kalkhambkar, G.M. Kulkarni, *J. Appl. Electrochem.* 38 (2008) 279.
21. E. Machnikova, K.H. Whitmire, N. Hackerman, *Electrochim. Acta* 53 (2008) 6024.
22. S.A. Ali, H.A. Al-Muallem, M.T. Saeed, S.U. Rahman, *Corros. Sci.* 50 (2008) 664.
23. S.A. Ali, M.T. Saeed, S.U. Rahman, *Corros. Sci.* 45 (2003) 253.
24. D. Wahyuningrum, S. Achmad, Y.M. Syah, Buchari, B. Bundjali, B. Ariwahjoedi, *Int. J. Electrochem. Sci.* 3 (2008) 154.
25. M. Benmessaoud, K. Es-Salah, N. Hajjaji, H. Takenouti, A. Srhiri, M. Ebentouhami, *Corros. Sci.* 49 (2007) 3880.
26. S.A.M. Refaey, F. Taha, A. M. Abd El-Malak, *Int. J. Electrochem. Sci.* 1 (2006) 80.
27. L. Larabi, O. Benali, S.M. Mekelleche, Y. Harek, *Prog. Org. Coat.* 253 (2006) 1371.
28. N. Kaniskan, C. Ogretir, *J. Mol. Struct.* (Theochem) 584 (2002) 45.
29. M. Özcan, İ. Dehri, *Progress in Organic Coatings* 51 (2004) 181.
30. D.Q. Zhang, L.W. Gao, G.D. Zhou *Corros. Sci.* 46 (2004) 3031
31. G. Gao, C. Liang, *Eletrochim. Acta* 52 (2007) 4554.
32. M. J. Frisch, G. W.Trucks, H. B.Schlegel, G. E.Scuseria, M. A.Robb, J. R. Cheeseman, J. A., Jr. Montgomery, T.Vreven, K. N.Kudin, J. C.Burant, J. M. Millam, S. S.Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A.Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, Revision B.3; Gaussian, Inc.: Pittsburgh, PA, 2003.
33. A.D. Becke, *J. Chem. Phys*. 98 (1993) 5648.
34. C. Lee, W. Yang, R. G.Parr, *Phys. Rev. B* 37 (1988) 785.
35. S. Miertus, E. Scrocco, J. Tomasi, J. Chem. Phys. 55 (1981) 117.
36. V. Barone, M. Cossi, J. Tomasi, *J. Chem. Phys.* 107 (1997) 3210.
37. M.A. Thompson, M.C. Zerner, *J. Am. Chem. Soc.* 113 (1991) 8210.
38. M.A. Thompson, E.D. Glendening, D. Feller, *J. Phys. Chem.* 98 (1994) 10465.
39. M.A. Thompson, G.K. Schenter, *J. Phys. Chem.* 99 /1995) 6374.
40. M.A. Thompson, J. *Phys. Chem.* 100 (1996) 14492.
41. R.G. Parr, W. Yang, Density functional theory of atoms and molecules. New York: Oxford University Press; 1989]:
42. M. Galván, A. Vela, J. L. Gázquez, *J. Phys. Chem.* 92 (1988) 6470.
43. R.G. Parr, L. Szentplay, S. Liu, *J. Am. Chem. Soc.* 121 (1999), 1922.
44. R.G. Parr, W. Yang, P.W. Ayers, M. Levy, *Theor. Chem. Acc.* 103 (2000), 353

45. K. Fukui, The world of quantum chemistry Daudel and Pullman ed USA. Proceedings of the first international congress of quantum chemistry held at menton 1974. p. 113–141.
46. M. Galván, R. Vargas, *J. Phys. Chem.* 96 (1992) 1625.
47. J. Cioslowsky, M. Martinov, S.T. Mixon, *J. Am. Phys. Chem.* 97 (1993) 10948.
48. F. Profit, R. Vivas-Reyes, A. Peeters, C. Alsenoy, P. J. Geerling, *Comp. Chem.* 24 (2003) 463.
49. W. Yang, W.J. Mortier, *J. Am. Chem. Soc.* 108 (1986) 5708.
50. F. Bentiss, M. Lebiri, H. Vezin, M. Lagrenee, *J. Matt. Chem. Phys.* 87 (2001) 18.
51. H. Wang, X. Wang, L. Wang, A. Liu, *J. Mol. Model* 13 (2007) 147.
52. N.K. Allan, *J. App. Surf. Sci.* 253 (2007) 4570.
53. M. Sahin, G. Gece, F. Kaerci, S. Bligic, J. *Appl. Electrochem.* 38 (2008) 809.
54. V.S. Sastri, J. R. Perumareddi, *Corros. Sci.* 50 (1994) 432.
55. J. Cruz, E. García-Ochoa, M. Castro. *J. Electrochem. Soc.* 150 (2003) B26.
56. F. Bentis, M. Traisnel, H. Vezin, H.F. Hildebrand, M. Lagrenée. *Corros. Sci.* 46 (2004) 2781.
57. H. Wang, X. Wang, H. Wang, L. Wang, A. Liu, *J. Mol. Model* 13 (2007) 147.
58. N.K. Allam, *Appl. Surf. Sci.* 253 (2007) 4570.
59. L.M. Rodríguez-Valdez, W. Villamisar, M. Casales, J.G. González-Rodríguez, A. Martínez-Villafañe, L. Martínez, D. Glossman-Mitnik. *Corros. Sci.* 48 (2006) 4053.
60. V. F. Ekpo, P. C. Okafor, U. J. Ekpe, E. E. Ebenso, *Int. J. Electrochem. Sci.*, 6 (2011) 1045.
61. N.O. Eddy, B. I. Ita , N.E. Ibisi, E.E. Ebenso, *Int. J. Electrochem. Sci.*, 6 (2011) 1027.
62. E.E. Ebenso, I.B. Obot, *Int. J. Electrochem. Sci.*, 5 (2010) 2012.
63. B.B. Ivanova, L.I. Pindeva, *J. Mol. Struct.*, 797. (2006) 144.