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Theoretical Study of a New Group of Corrosion Inhibitors

B. Gómez,*,[†] N. V. Likhanova,[†] M. A. Domínguez Aguilar,[†] O. Olivares,[‡] J. M. Hallen,[‡] and J. M. Martínez-Magadán[†]

Programa de Ingeniería Molecular, Instituto Mexicano del Petróleo, Eje Lázaro Cárdenas 152,
Col. San Bartolo de Atepehuacan, Gustavo A. Madero, México 07730 D.F., and Departamento de Ingeniería
Metalúrgica, Instituto Politécnico Nacional-ESIQIE, Apdo. Postal 75-876, México 07300 D.F.

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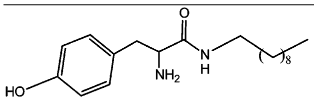
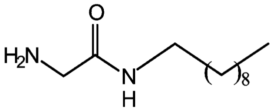
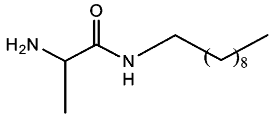
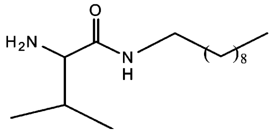
In the present work, the molecular interactions of four amino acid compounds were simulated through the density functional theory (DFT) indexes to study their inhibitive properties. The prototype inhibitors previously synthesized 2-amino-*N*-decylacetamide (G), 2-amino-*N*-decylpropionamide (A), 2-amino-*N*-decyl-3-methyl-butyramide (V), and 2-amino-*N*-decyl-3-(4-hydroxyphenyl)propionamide (T) were used to test the accuracy of this calculation. The generalized gradient approximation (GGA) was the ab initio approach used to optimize the ground state of the molecules. The simulation of molecular dynamics with force field (AMBER) was calculated to obtain the interaction energy between the metallic surface and the inhibitor molecules. A strong correlation of the global and local indexes with the inhibiting capacity was observed. The inhibitive properties of compounds on mild steel in an aqueous hydrochloric acid solution agreed well with those derived from the reactivity and selectivity indexes in gaseous phase.

1. Introduction

An important method of protecting metallic materials against deterioration due to corrosion is by the use of 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[2,3] that adsorption depends mainly on the physicochemical properties of the inhibitor group, such as functional groups, electronic density at the donor atom,[2] π-orbital character, and the molecular electronic structure.[3] The relationship between the organic compound structure, the molecular adsorption processes and their inhibitive efficiency on metals has attracted intensive research on inhibitor compounds. Owing to the new environmental restrictions, searching for substitute compounds has led to the use of amino acids, environmental friendly compounds that have been effectively employed as inhibitors in many corrosive systems.[4] In this regard, amino acids represent a promising alternative for the design of "green" corrosion inhibitors;[5] biodegradability will satisfy the ever increasing requirements of environmental regulation, which are currently imposed on the development of cleaner chemical inhibitors. The development of efficient inhibitors has been done by empirical knowledge based on the macroscopic physicochemical properties of compounds. 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.

TABLE 1: Chemical Formulas of the Investigated Compounds

Structure	Common name	IUPAC name	Abbreviation
	Decylamide of tyrosine	2-Amino-*N*-decyl-3-(4-hydroxy-phenyl)-propionamide	T
	Decylamide of glycine	2-Amino-*N*-decyl-acetamide	G
	Decylamide of alanine	2-Amino-*N*-decyl-propionamide	A
	Decylamide of valine	2-Amino-*N*-decyl-3-methyl-butyramide	V

The density functional theory (DFT)[6] has been found to be successful in providing insights into the chemical reactivity and selectivity, in terms of global parameters such as electronegativity[7] (χ), hardness[8] (η) and softness[6] (S), and local ones such as the Fukui function[9] ($f(\vec{r})$) and local softness[10] ($s(\vec{r})$). Thus, for an N-electron system with total electronic energy (E) and an external potential ($\upsilon(\vec{r})$); chemical potential[7] (μ) known as the negative of electronegativity (χ), has been defined as the first derivative of the E with respect to N at $\upsilon(\vec{r})$:[11]

$$\mu = -\chi = \left(\frac{\partial E}{\partial N}\right)_{\upsilon(\vec{r})} \tag{1}$$

Hardness (η) has been defined within the DFT as the second derivative of the E with respect to N at $\upsilon(\vec{r})$:[12]

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{\upsilon(\vec{r})} \tag{2}$$

Recently, Parr et al.[13] have introduced an electrophilicity index (ω) defined as

$$\omega = \frac{\mu^2}{2\eta} \tag{3}$$

This was proposed as a measure of the electrophilic power of

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* Author for correspondence. E-mail address: bgomez@imp.mx.
[†] Instituto Mexicano del Petróleo.
[‡] Instituto Politécnico Nacional-ESIQIE.

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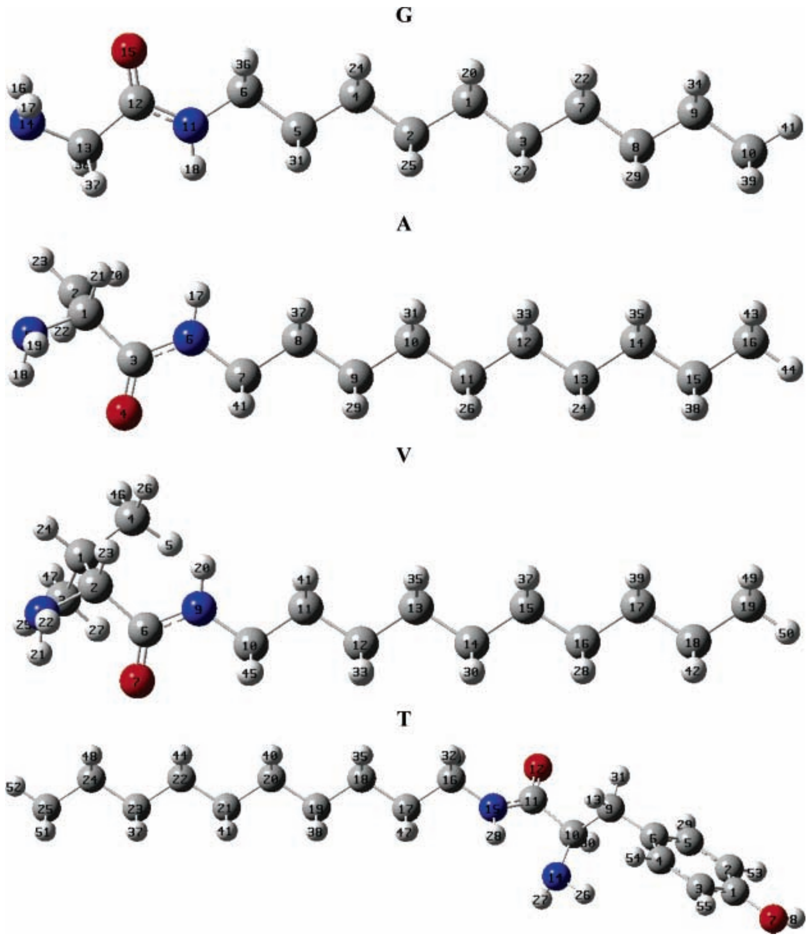


Figure 1. Optimized structures: (a) 2-amino-*N*-decylacetamide; (b) 2-amino-*N*-decylpropionamide; (c) 2-amino-*N*-decyl-3-methylbutyramide; (d) 2-amino-*N*-decyl-3-(4-hydroxyphenyl)propionamide.

a molecule. Local quantities such as the Fukui function and local softness ($s(\vec{r})$) are necessary in understanding the site selectivity. The Fukui function is defined as[9]

$$f(\vec{r}) = \left(\frac{\partial^2 E}{\partial N \partial v(\vec{r})}\right) = \left(\frac{\delta \mu}{\delta v(\vec{r})}\right) = \left(\frac{\partial \rho}{\partial N}\right)_{v(\vec{r})} \tag{4}$$

Three different types of the Fukui function[9] ($f(\vec{r})$) have been defined on the basis of the discontinuity in chemical potential at integer N:

$$f(\vec{r})^+ = \left(\frac{\partial \rho}{\partial N}\right)^+_{v(\vec{r})} \cong \rho(\vec{r})_{\mathrm{LUMO}}$$

$$f(\vec{r})^- = \left(\frac{\partial \rho}{\partial N}\right)^-_{v(\vec{r})} \cong \rho(\vec{r})_{\mathrm{HOMO}}$$

$$f(\vec{r})^0 = \frac{1}{2}(f(\vec{r})^+ + f(\vec{r})^-) \tag{5}$$

Associated local softness can be written as[10]

$$s(\vec{r})^\alpha = S f(\vec{r})^\alpha \qquad \alpha = +, -, \text{and } 0 \tag{6}$$

where $\alpha = +, -$, and 0 for nucleophilic, electrophilic and radical attack, respectively, and the global softness is given by[6]

$$S = \frac{1}{\eta} \tag{7}$$

The Fukui functions and softness have been successfully applied as a chemical reactivity criterion in different reaction processes.

On the other hand, the topological analysis of the electron localization function (ELF) of Becke and Edgecombe[14] provides an elegant partition of the molecular space into basins of attractors, which can be consistently interpreted on the basis of simple ideas of chemical bonding based on the Pauli exclusion principle. This methodology has proven to be a practical tool to describe the chemical bonding nature in several stationary systems[15−18] as well as in some simple chemical reaction processes.[19] Several interesting issues of chemical reactivity and selectivity have been also addressed with this increasingly useful tool.[20] The local function ELF($\vec{r}$) has been defined and interpreted in terms of the excess of local kinetic energy density due to Pauli repulsion, $T(\rho(\vec{r}))$, and the Thomas−Fermi kinetic energy density $T(\rho(\vec{r}))$.[16,17]

$$\mathrm{ELF}(\vec{r}) = \frac{1}{1 + \left[\dfrac{T(\vec{r})}{T_h(\vec{r})}\right]^2} \tag{8}$$

These quantities, when evaluated for a single determinant wave function based on the Hartree−Fock (HF) or Kohn−Sham (KS) orbital ($\varphi_i(\vec{r})$), can be written straightforward as follows:

$$T(\vec{r}) = \frac{1}{2}\sum_i |\nabla \varphi_i(\vec{r})|^2 - \frac{1}{8}\frac{|\nabla \rho(\vec{r})|^2}{\rho(\vec{r})} \tag{9}$$

$$T_h(\vec{r}) = 2.871\rho(\vec{r})^{5/3} \tag{10}$$

$$\rho(\vec{r}) = \sum_i |\varphi_i(\vec{r})|^2 \tag{11}$$

The key term in the ELF is the function $T(\vec{r})$ of eq 10, which

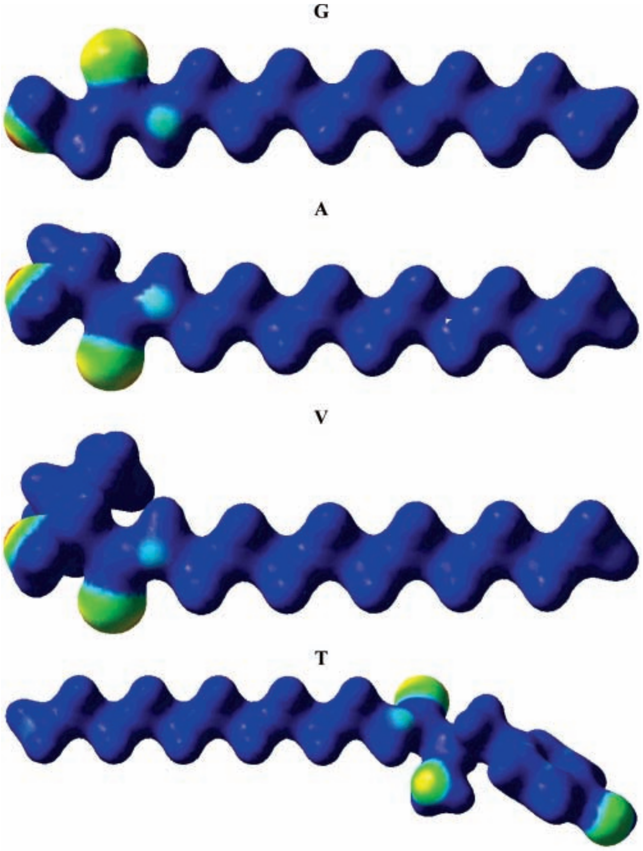


Figure 2. Total electronic density with a value of isosurface of 0.04 for G, A, V and T.

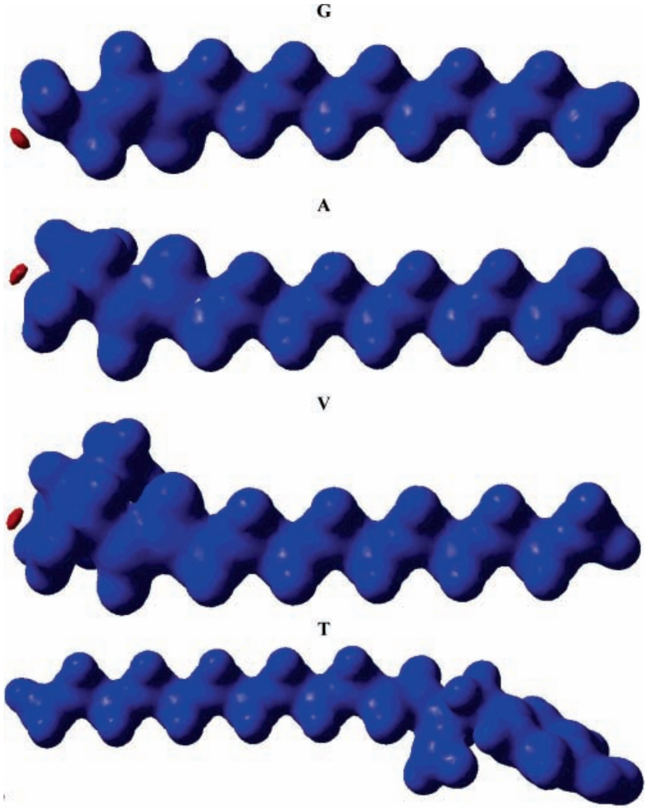


Figure 3. Electrostatic potential with a value of isosurface of 0.1 for G, A, V and T.

represents the excess of kinetic energy density due to the Pauli exclusion principle. The final form of the ELF has a high value,

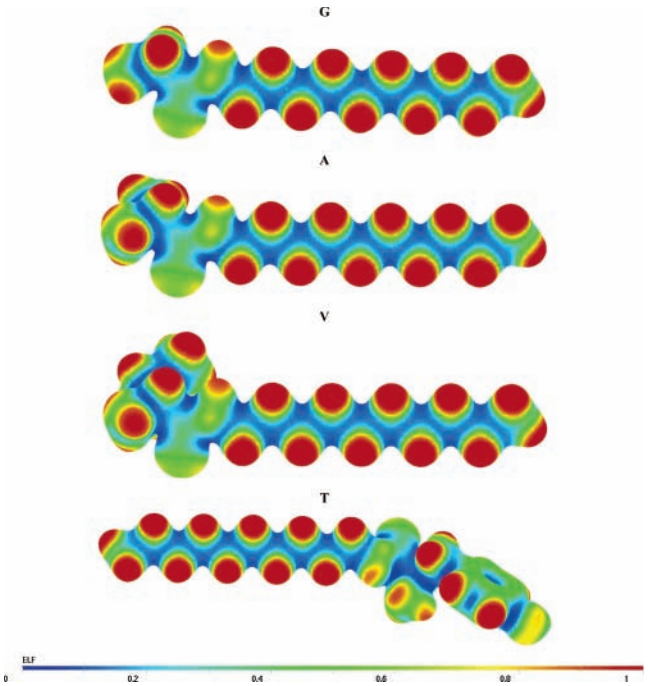


Figure 4. Electron localization function of **G**, **A**, **V** and **T**.

which represents a space region where it is likely to find an electron pair. The gradient field of the ELF function provides the basins of attractors, whose properties can then be interpreted in connection with the relevant chemical bonding characteristics. These properties have been related to the intuitive concepts of localization and delocalization of the electron density[21] through a standard population topological analysis.

The aim of this work was to measure the global and local reactivity indexes of prototype molecules, in combination with the electron localization function to determine the molecular reactivity and selectivity of the chemical bonding during the corrosion process. These indexes were useful to evaluate the inhibitive capability of the following amino acids (Table 1) in their ground states: 2-amino-*N*-decylacetamide (G), 2-amino-*N*-decylpropionamide (A), 2-amino-*N*-decyl-3-methylbutyramide (V) and 2-amino-*N*-decyl-3-(4-hydroxyphenyl)propionamide (T). Both sets of indexes assisted in the analysis of chemical reactivity, specifically in those aspects related to the reaction mechanism. In addition, the interaction of the inhibitor molecule with the steel surface on the first three iron layers was calculated to determine the interaction energy between them. A previous work on the inhibitive capability of these four new amides of α-amino acids has been recently published.[22] It appears that prototype inhibitors are capable of delaying metallic corrosion of carbon steel in aqueous 1.0 M HCl. Inhibitor efficiency was evaluated by weight loss measurements and polarization scans and supported by XPS analysis.

2. Computational Details

Equilibrium geometries in the ground state were optimized at the generalized gradient approximation level of theory. Becke[23] exchange (B) and Lee, Yang and Parr[24] functional correlations (LYP) were used for this purpose. All of the studied inhibitors were obtained by optimization within a density functional framework using a DZVP[25] basis set in combination

TABLE 2: Total Energy,[a] Chemical Potential (μ),[b] Hardness (η),[b] Softness (S),[c] and Electrophilicity (ω)[b] of the Four Molecules with Inhibitor Properties Studied in the Present Work

species	energy	μ	η	S	ω
G	−657.4170	−2.65	4.95	0.20	0.35
A	−696.7090	−2.63	4.90	0.20	0.35
V	−775.2866	−2.54	4.91	0.20	0.33
T	−1002.9091	−3.11	3.97	0.25	0.61

[a] In au. [b] In eV. [c] In 1/eV.

TABLE 3: Fukui Functions and Local Softness Values for a Nucleophilic and Electrophilic for 2-Amino-*N*-decylacetamide (G)

number	atom	$f^+(r)$	$f^-(r)$	$S^+(r)$	$S^-(r)$
6	C	0.00	0.01	0.00	0.00
11	N	0.11	0.03	0.02	0.01
12	C	0.52	0.08	0.10	0.02
13	C	0.02	0.07	0.00	0.01
14	N	0.00	0.48	0.00	0.09
15	O	0.24	0.28	0.05	0.06
35	H	0.02	0.00	0.00	0.00
36	H	0.01	0.00	0.00	0.00
37	H	0.03	0.01	0.01	0.00
38	H	0.03	0.01	0.01	0.00

with an auxiliary functions (GEN-A2*) for the electron density. Hardness (η) was calculated as follows:

$$\eta = \frac{\mathrm{IP} - \mathrm{EA}}{2} \tag{12}$$

This definition was derived from eq 2 by the finite difference approximation, where IP is the ionization potential and EA is the electron affinity. The condensed Fukui functions were calculated as[26]

$$f_k^{\alpha} = \sum_{\upsilon \in k}^{\mathrm{AO}} |C_{\upsilon\alpha}|^2 + \sum_{x \neq \upsilon}^{\mathrm{AO}} C_{x\alpha} C_{\upsilon\alpha} S_{x\upsilon} \qquad \alpha \equiv +, 0, - \tag{13}$$

where $\{C_{\upsilon\alpha}\}$ are the frontier molecular orbital coefficients and $\{S_{x\upsilon}\}$ are the atomic orbital overlap matrix elements. Local softness was calculated from eqs 6 and 7 with above definitions of f_k^{α} and S. The evaluation of the topological analysis of ELF defined in eq 8 has been carried out by using the TOPMOD series of programs.[27] The graphic visualization of results was done with the VUChem[28] and GaussView[29] tools. All calculations of optimization were accomplished with the deMon2003 computational package.[30] Additionally, single point calculations were done by using the GAUSSIAN98[31] computational package.

The interaction of prototype inhibitors with the metallic surface was studied by calculating the simulation of molecular dynamics using the force fields type AMBER.[32] To maintain the structure of iron surface frozen, this was restricted to the dimensions of 29.37 × 29.37 × 5.34 Å that contained a total of 432 iron atoms. The inhibitor was left to freely interact with the iron surface for a period of time to allow a chemisorption process to occur. The interaction energy was then calculated as

$$\Delta E_i = E_{\mathrm{bond}} - E_{\mathrm{nobond}} \tag{14}$$

The molecular dynamic calculations were done at a simulation temperature of 298.15 K for a testing time period of 50 ps. These calculations were then accomplished with the HyperChem7[33] computational package.

3. Results and Discussion

The optimized structures for the four inhibitors (G, A, V and T) in their respective ground state are presented in Figure 1.

TABLE 4: Fukui Functions and Local Softness Values for a Nucleophilic and Electrophilic for 2-Amino-*N*-decylpropionamide (A)

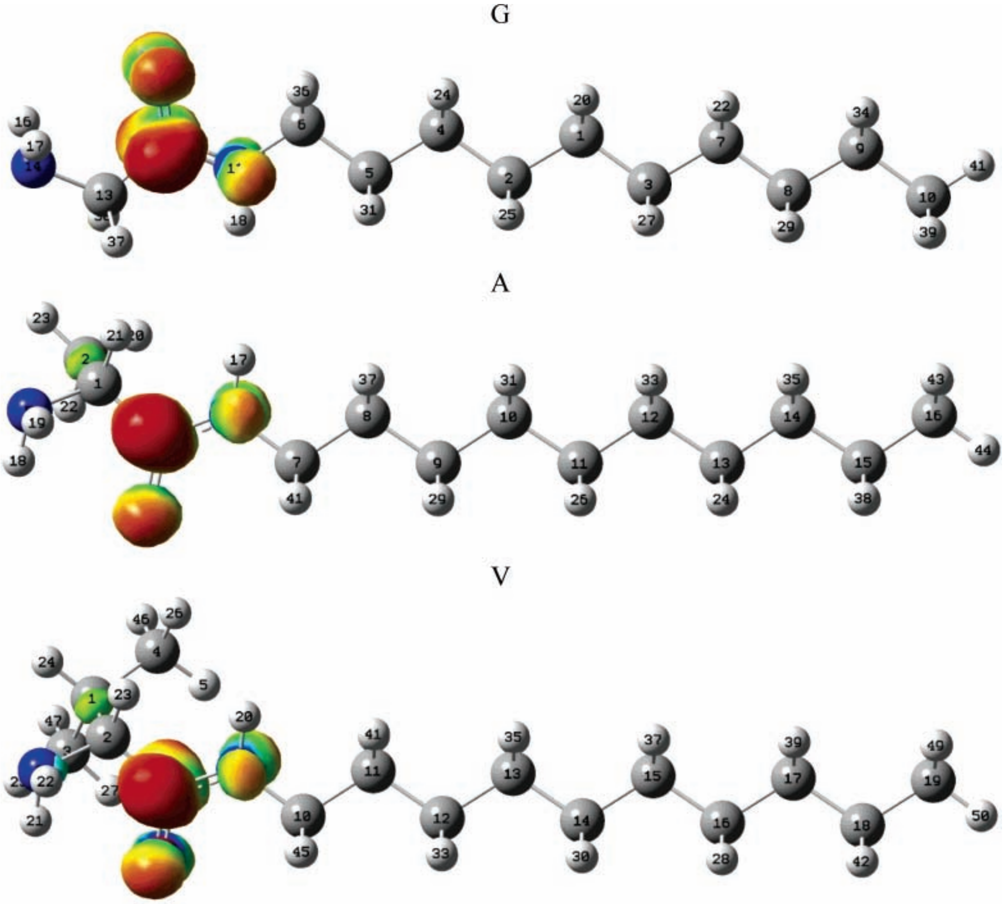
number	atom	$f^+(r)$	$f^-(r)$	$S^+(r)$	$S^-(r)$
1	C	0.06	0.07	0.01	0.01
2	C	0.03	0.02	0.01	0.00
3	C	0.50	0.07	0.10	0.01
4	O	0.23	0.29	0.05	0.06
5	N	0.01	0.46	0.00	0.09
6	N	0.11	0.03	0.02	0.01
7	C	0.00	0.01	0.00	0.00
17	H	0.01	0.00	0.00	0.00
18	H	0.00	0.01	0.00	0.00
19	H	0.01	0.01	0.00	0.00
21	H	0.02	0.01	0.00	0.00
23	H	0.01	0.01	0.00	0.00
40	H	0.01	0.00	0.00	0.00
41	H	0.02	0.00	0.00	0.00

TABLE 5: Fukui Functions and Local Softness Values for a Nucleophilic and Electrophilic for 2-Amino-*N*-decyl-3-methylbutyramide (V)

number	atom	$f^+(r)$	$f^-(r)$	$S^+(r)$	$S^-(r)$
1	C	0.02	0.02	0.00	0.00
2	C	0.05	0.07	0.01	0.01
6	C	0.49	0.06	0.10	0.01
7	O	0.22	0.28	0.05	0.06
8	N	0.01	0.47	0.00	0.10
9	N	0.12	0.04	0.02	0.01
10	C	0.01	0.01	0.00	0.00
20	H	0.01	0.00	0.00	0.00
21	H	0.00	0.01	0.00	0.00
22	H	0.00	0.01	0.00	0.00
23	H	0.02	0.01	0.00	0.00
24	H	0.02	0.01	0.00	0.00
44	H	0.01	0.00	0.00	0.00
45	H	0.02	0.00	0.01	0.00

The vibrational frequency calculations for the four cases did not show any negative value in the Hessian matrix; this fact confirms that the studied molecules reached their respective ground state. In the four cases, they exhibit an aliphatic side chain of 10 carbon atoms together with a change in the substituent group, for instance, the α-carbon with hydrogen for G, methyl for A, 2-propyl for V and 4-hidroxyphenyl for T.

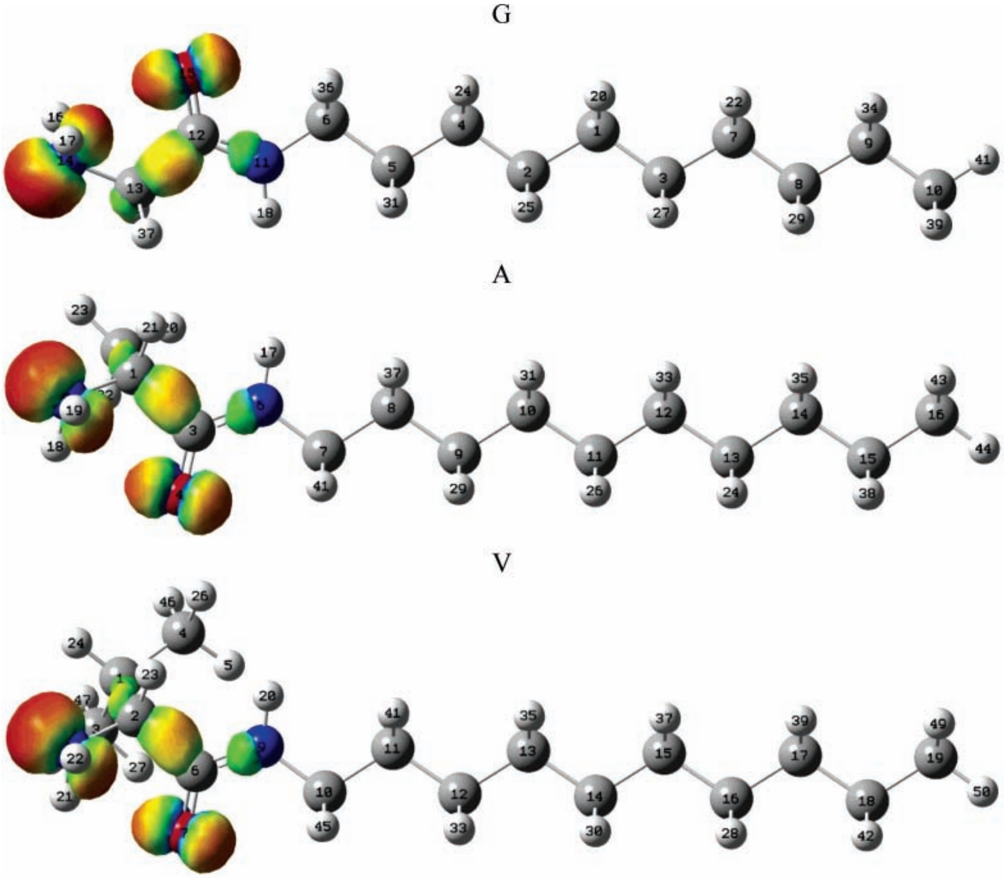
3.1. Global Reactivity. Figure 2 shows the total electronic density for an isosurface value of 0.04; the greater charge density is displayed both on the terminal amino group and on the carbonyl group in the four cases. In the first three compounds, the proton affinity is clearly favored toward the amino group ends. In previous studies, Contreras et al.[34] demonstrated that when there is competition for proton affinity between the groups amino and carbonyl, an initial protonation takes place over the amino group followed by an intramolecular rearrangement of proton to the carbonyl group.[35] As the action of these compounds takes place in acid environment, it is very likely that the protonation process may occur by a transition state quite similar to the TS-3 of ref 35. In this way, the terminal amino group is exposed any time to interact with the metallic surface. These observations are clearly reinforced from Figure 3, where it is depicted the electrostatic potential for an isosurface of 0.1. In the first three molecules a negative charge exists on the terminal amino groups, whereas the negative charge does not appear on the terminal amino group of the fourth molecule. Figure 4 displays the ELF; in the four cases it can be observed that the lone-pair electrons on nitrogen atom result in a high value of ELF. This indicates that a pair of free electrons is always available on this atom to interact with a metallic surface. It can also be distinguished that the alkylic chains display an ELF on the C−H bond of aliphatic chain. In the fourth molecule (T),


G

A

V

Figure 5. Fukui function for a nucleophilic attack with an isosurface value of 0.005 for G, A and V.


G

A

V

Figure 6. Fukui function for a electrophilic attack with an isosurface value of 0.005 for G, A and V.

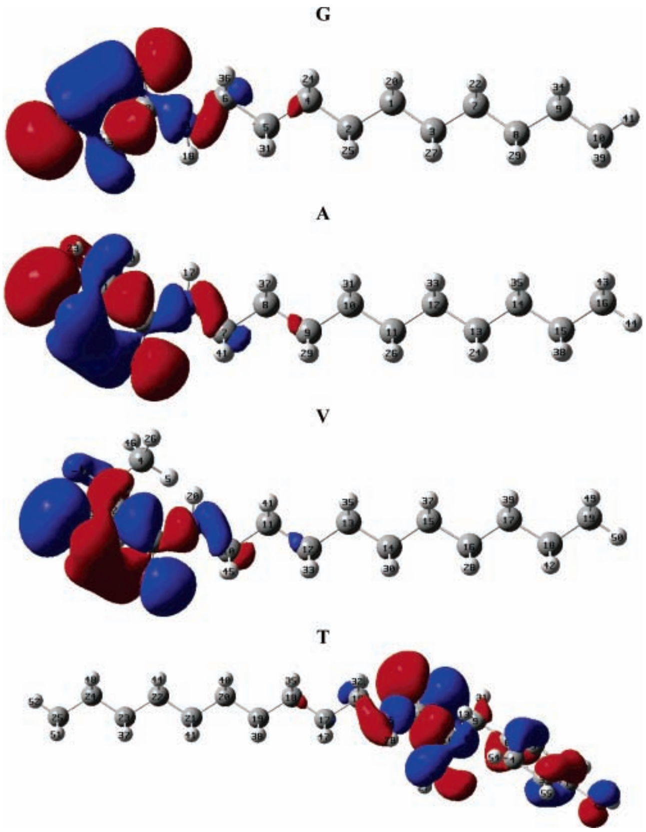


Figure 7. Highest occupied molecular orbital (HOMO) energy with a value of isosurface of 0.02 for G, A, V and T.

the resonant electrons on the phenylic ring are clearly observed at about 0.5 of the electron localization function. The pair of free electrons pertaining to the hydroxyl group of the phenyl ring is not clearly defined on the oxygen atom; this is probably ascribed to the resonance effect of π-electrons located at the phenyl ring.

Table 2 summarizes the total energy, the electronic chemical potential, the chemical hardness, the softness, and the electrophilicity of the four compounds studied in the present work. It can be observed (Table 2) that T is the compound that displays the greater reactivity in relationship to the other ones, as a result of the high value of global softness. Furthermore, compound T exhibits a high value of electrophilicity, which confirms the high capacity of the molecule to accept electrons. For the other three molecules, the differences of the global index values remain essentially constant with minor variations. When the difference of the global indexes of reactivity is small or almost constant, the molecular reactivity cannot be predicted, so that it is necessary to take into account an additional criterion to determine the inhibitive capacity of these three molecules. As the molecules display similar global indexes, the reactivity is transferred to the atomic centers, which generate site selectivity in each one of the molecules when they participate in the corrosion process.

3.2. Local Selectivity. In Tables 3−5, the values of the Fukui functions and local softness for a nucleophilic and electrophilic attack are displayed for the three remaining inhibitors (G, A and V, respectively). For a nucleophilic attack, the most reactive site is on the carbon atom of the carbonyl functional group; the order in the site selectivity is then defined as G > A > V (Figure 5). The values of the Fukui functions when molecules undergo an electrophilic attack indicate that it will happen on the nitrogen at the terminal amino group for all cases. When these three values are compared, the order in the site selectivity is as follows: G > V > A (Figure 6).

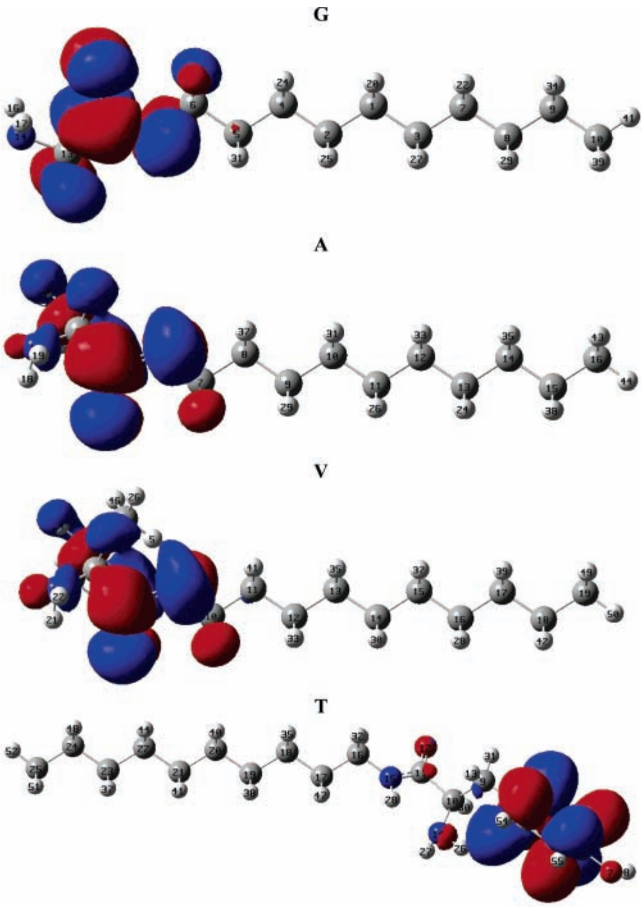


Figure 8. Lowest unoccupied molecular orbital (LUMO) energy with a value of isosurface of 0.02 for G, A, V and T.

TABLE 6: The Interaction Energy of Prototype Molecules When the Inhibitors Interact with a Three Layer Iron Surface

specie	ΔE_i (kcal/mol)
G	73.69
A	88.03
V	88.57
T	83.22

In Figure 7 is displayed the graphic form of the highest occupied molecular orbital (HOMO) and in Figure 8, the lowest unoccupied molecular orbital (LUMO) of the molecules under study. From these figures, it can be observed that the compounds exhibit an effect of retrodonation because the molecular coefficients are relatively high for the same centers in both the HOMO and LUMO. For the three former molecules G, A and V the reactivity is presented on the functional group regions. The exception is the fourth molecule (T), which presents a clear contribution of ρ-orbitals pertaining to the phenyl ring on the LUMO.

3.3. Molecular Dynamic. Table 6 presents the values of the interaction energies for the four compounds studied herein; this energy was calculated by the molecules interacting on the three layer iron surface. In accordance with calculations, compound G presented the lowest value of 73.69 kcal/mol, followed by T with 83.22 kcal/mol and A with 88.03. Finally, the prototype inhibitor V displayed the highest value of 88.57 kcal/mol. Figure 9 displayed the average location of the four molecules on the steel surface at room temperature.

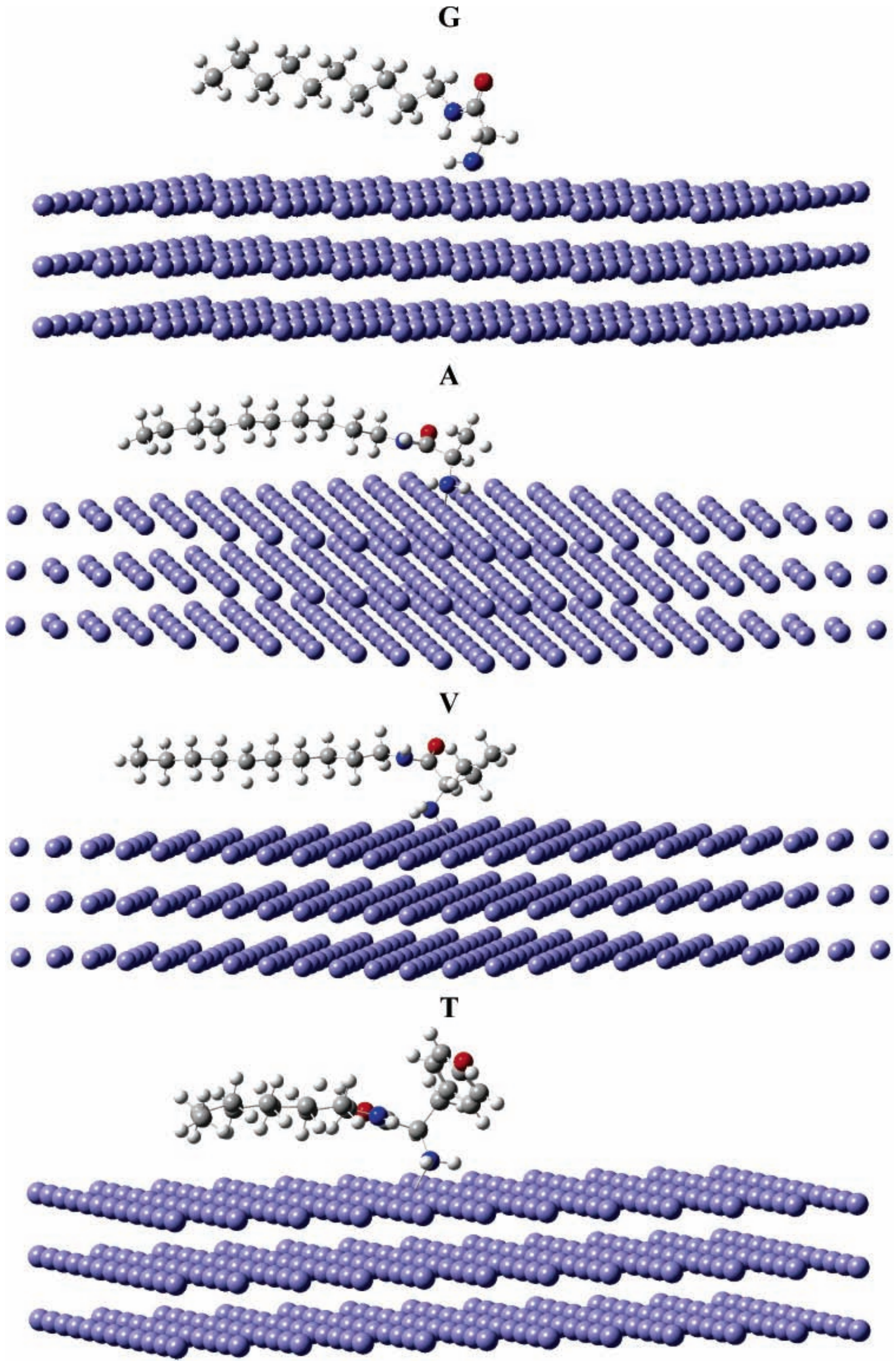


Figure 9. Average location of inhibitor prototype molecules on steel surface for G, A, V and T.

From the simulation of the molecular dynamic, it is clearly observed that if only the classic interactions (force field) are considered, the compound with greater action as inhibitor would be G and T. If, additionally, the quantum mechanics interactions (global indexes, retrodonation effect) are included, the compound with the greatest affinity to the steel surface would be inhibitor T. When the Fukui functions and local softness (local indexes) are analyzed, it is expected that G will be more reactive by site selectivity than either A or V. Moreover, these two molecules exhibited a comparable global reactivity and site selectivity, so that their efficiencies as corrosion inhibitors have to be similar. This information is in agreement with the values of interaction energies between the molecules and steel surface obtained from molecular dynamics for these two compounds (A and V). However, the interaction observed for all the molecules studied was a retrodonation type, this by the form of the frontier molecular orbital (HOMO and LUMO). The theoretical results obtained herein are in complete agreement with the experimental results reported elsewhere.[22]

4. Concluding Remarks

The compounds derived from the amino acids with an aliphatic chain of 10 carbon atoms display inhibitive properties against the corrosion process of carbon steel. The global and local reactivity indexes, derived from the density functional theory, indicate that the inhibitive capacity of prototype molecules is as follows: T > G > A > V. The nature of the inhibitive interactions with the metallic surface can be characterized by quantum mechanics correlations, because the reactivity and selectivity indexes determined in the gaseous phase suggest that the information obtained herein is in complete agreement with that derived from experimental results.

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