Computational Study of Some Amino Acid Derivatives as Potential Corrosion Inhibitors for Different Metal Surfaces and in Different Media

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Quantum chemical calculations and molecular dynamics studies have been performed on five amino acid derivatives, namely aminoheptadecanoic acid, aminohexadecanoic acid, aminopentadecanoic acid, aminotetradecanoic acid and aminotridecanoic acid to investigate their possible role as corrosion inhibitors for metal surfaces in different media. Quantum chemical calculations were performed to elucidate and compare the molecular reactivity parameters of these compounds while molecular dynamics studies were meant to investigate their binding properties on different metal surfaces. The results of the study indicate that amino acid derivatives have high tendency to interact with the metal surface by donating electrons through their amino groups and accepting electrons through their carboxylic acid group. Molecular dynamics studies have shown that the adsorption of the inhibitor molecule depends on the nature of the metal surface and the media.

1. INTRODUCTION

Metal surfaces are extensively used in a variety of industrial applications such as petroleum, textile and marine industries as a component of pumps or valves that carry various types of substances. However some of these substances are highly corrosive and include such solutions as hydrochloric acid [1]. For instance, in the petroleum industry hydrochloric acid solutions are widely utilized for oil

well acidizing, while in marine industries hydrochloric acid is largely used for pickling purposes [2]. The corrosion of metal surfaces causes huge financial damages to the industries annually, what has lead to an increase in the search for substances that can slow down or prevent corrosion rate. Among the various possibilities utilized to prevent corrosion is the use of substances that adsorb on the metal-solution interface, thus blocking the metal from coming into contact with the corrosive solution. Such substances that adsorb onto the surface of the metal both physically and chemically are called corrosion inhibitors [3] and they range from various sources, including organic molecules, ionic liquids, amino acid derivatives, etc [4–8]. Although such materials cannot protect the metal indefinitely, they decrease the rate of metal dissolution, thereby lengthen the time-span for the use of the metals.

The efficiency of a corrosion inhibitor depends strongly on its adsorption on the metal surface. However, such a process involves many influencing factors beside the inhibitor, such as the nature of the metal, the environment and the electrochemical potential at the metal-solution interface [9]. Therefore a careful study of the adsorption process of an inhibitor on the metal surface needs to take into consideration all the necessary factors. In the selection of potential corrosion inhibitors, the most interesting factors to take into consideration include the geometric properties and electronic properties of the compounds. The geometry of the molecule has strong influence in the adsorption of the inhibitor on the metal surface as it informs of the optimal way by which the inhibitor might cover the metal surface. Compounds that have planar geometry often have higher inhibition efficiency than corresponding compounds with less planar geometry [10–12].

While geometric parameters inform about the surface coverage of the metal by the inhibitor, electronic parameters inform about the molecule's tendency to react and therefore bind on the metal surface. Such interactions between the inhibitor and the metal surface depend strongly on the electron density distribution in the inhibitor. Regions in the molecule that have high electron density would preferably donate electrons to the partially filled or the vacant *d* orbitals of the metal resulting in a donor-acceptor bond [13]. Molecules that have functional groups with high electron density have greater tendency to adsorb onto the metal surface, and include molecule with heteroatom functional groups (e.g., –C=O, –N=N and –NR$_2$, SH groups), conjugated π bonds and aromatic π systems [13]. The general trend in the inhibition efficiency of molecules containing heteroatoms is such that O < N < S < P [14]. This trend is probably related to the tendency of an atom to donate electrons and is therefore related to the electronegativity of the atom. Oxygen has the highest electronegativity value (3.44) and therefore it has the least tendency to donate electrons while phosphorus has the least electronegativity value (2.19) and has the highest tendency to donate electrons.

The search for effective corrosion inhibitors is an ongoing and an increasing number of classes of compounds are being explored for their corrosion inhibition potentiality in different corrosive environments. In this regard, we report in this work the possible role of five amino acid derivatives for corrosion inhibition against different metal surfaces *in vacuo*, in water solution, in aqueous hydrosulphuric acid (H$_2$S) and in aqueous hydrochloric acid solution. The selected amino acids include aminoheptadecanoic acid, aminohexadecanoic acid, aminopentadecanoic acid, aminotetradecanoic acid and aminotridecanoic acid. Density Functional Theory (DFT) method is utilized to obtain interesting molecular properties that are related to the reactivity of the compounds. The study was performed for

both neutral and the protonated species of the compounds. Molecular dynamics (MD) is utilized to investigate the binding properties of these compounds on different metal surfaces. The different metal surfaces include the isolated Fe (110), $FeCO_3$ (110), FeS_2 (110) and Fe_2O_3 (110) surface. Furthermore, the study was performed in different media; *in vacuo* for the fact that this is the preliminarily medium to start all calculations; in water solution, to investigate the effect of aqueous solution on the adsorption of the compounds; in H_2S, to investigate the binding strength in a weak acidic medium and in HCl solution to investigate the effect of the strong acid on the adsorption of the compound.

2. COMPUTATIONAL DETAILS

The study of the isolated compounds with density functional theory, were permed with the Becke's Three Parameter Hybrid Functional using the Lee-Yang-Parr correlation functional theory (B3LYP, [15]) using the 6-31G(d,p) basis set. Density functional theory (DFT) is largely utilized in the analysis of the characteristics of the inhibitor/metal surface mechanisms and in the description of the structural nature of the inhibitor on the corrosion process [16]. Chemical hardness (η), which measures of the resistance of an atom to a charge transfer [17], was estimated by using the equation:

$$\eta \cong -\tfrac{1}{2}\,(E_{HOMO} - E_{LUMO}) \tag{1}$$

and global chemical softness (σ), which describes the capacity of an atom or group of atoms to receive electrons [17], was estimated by using the equation:

$$\sigma = 1/\eta \cong -2/(E_{HOMO} - E_{LUMO}) \tag{2}$$

where in both equations, E_{HOMO} is the energy of the highest occupied molecular orbital (HOMO) and E_{LUMO} is the energy of the lowest unoccupied molecular orbital (LUMO).

The maximum number of electrons transferred (ΔN_{max}) in a chemical reaction is given by the equation [12]

$$\Delta N_{max} = \frac{\chi}{2\eta} \tag{3}$$

where χ is the electronegativity and it is estimated as

$$\chi \cong -\tfrac{1}{2}\,(E_{HOMO} + E_{LUMO}) \tag{4}$$

All optimization calculations were done using the Spartan 10 V1.01 program [18]. Optimized structures were drawn using the Spartan 10 V1.01 program.

The molecular dynamics simulations were performed by utilizing the Amorphous Cell, the Build Layer and the Discover Modules in Materials studio 6.0 program [19–23]. The Fe (110) and the Fe_2O_3 (110) surfaces were initially prepared and equilibrated utilizing the minimizer procedure in cooperated in Discover Module. The isolated metronidazole molecule was then build and optimized to determine the lowest energy structure. Using Amorphous Cell, the compound was inserted in a periodic box. The compound, in the periodic box, was then mounted onto the metal surfaces by using the Build Layer section in Materials Studio. The vacuum slab with 30 Å thicknesses was then built to separate the compound from the metal surface.The Molecular Dynamics simulation was performed at a the temperature of 298 K, using an NVT ensemble, with a time step of 0.1 fs and simulation time of 0.5 ps. For the study *in vacuo*, the binding energy on the metal surface was estimated following the

equation:

$$E_{binding} = E_{total} - (E_{surface} + E_{inhibitor})$$ (5)

where E_{total} is the total energy of the surface and inhibitor, $E_{surface}$ is the energy of the surface without the inhibitor, and $E_{inhibitor}$ is the energy of the inhibitor without the surface. Studies have shown that the adsorption energy of the inhibitors on the metal surface correlates with the inhibition efficiency exhibited by inhibitors [24].

3. RESULTS AND DISCUSSION

3.1 Neutral species of the amino acid derivatives

The geometries of the optimized lowest-energy conformer for each studied structure are shown in figure 1 together with the HOMO and the LUMO densities. The preferred geometry is one in which the carbon chain is linear and straight. The HOMO density shows that, for all the studied compounds, the amino group is the region with the highest density and therefore the highest tendency to donate electrons. This suggests that on interaction with the metal surface, the amino group would have the highest tendency to donate electron the to the vacant or partially filled *d* orbitals of the Fe atoms on the metal surface. The LUMO density is localized exclusively on the carboxylic acid group, indicating that this is the region with the highest tendency to accept electrons. The carbon skeletal chain of the molecules appear to have no contribution towards the donor-acceptor interactions.

Optimized structures

HOMO density

LUMO density

aminoheptadecanoic   aminohexadecanoic   aminopentadecanoic   aminotetradecanoic   aminotridecanoic
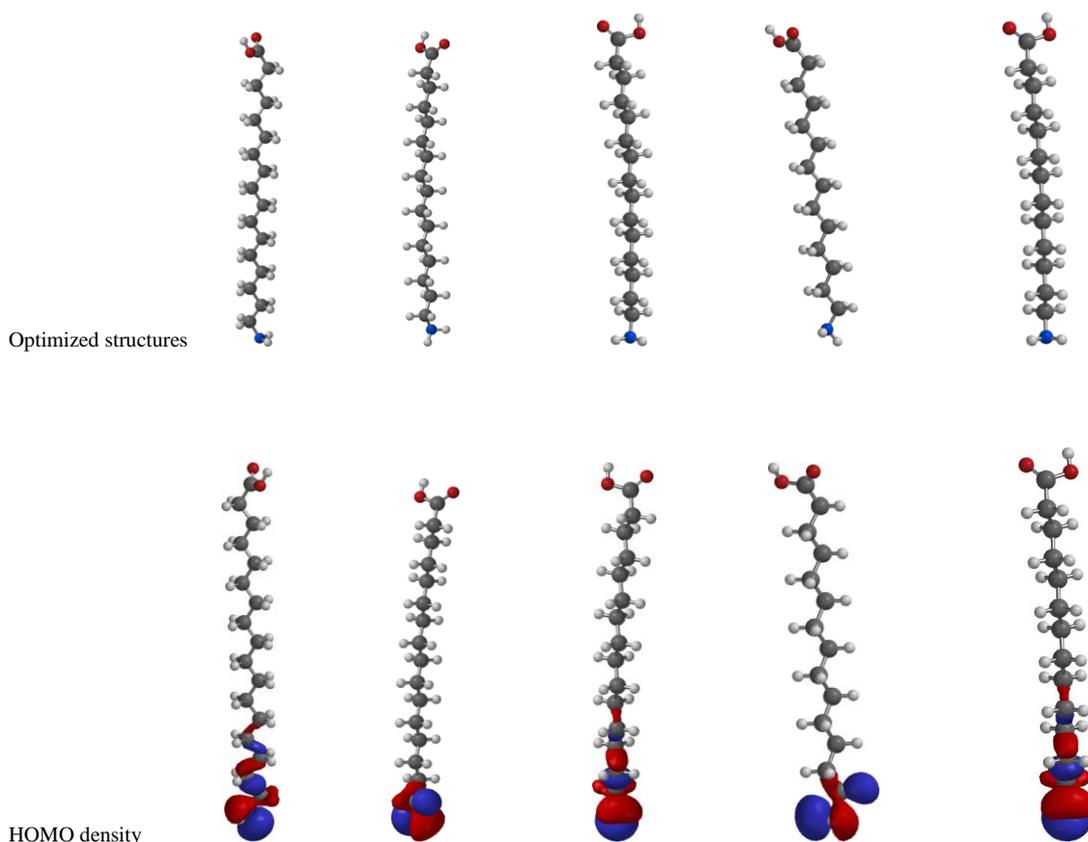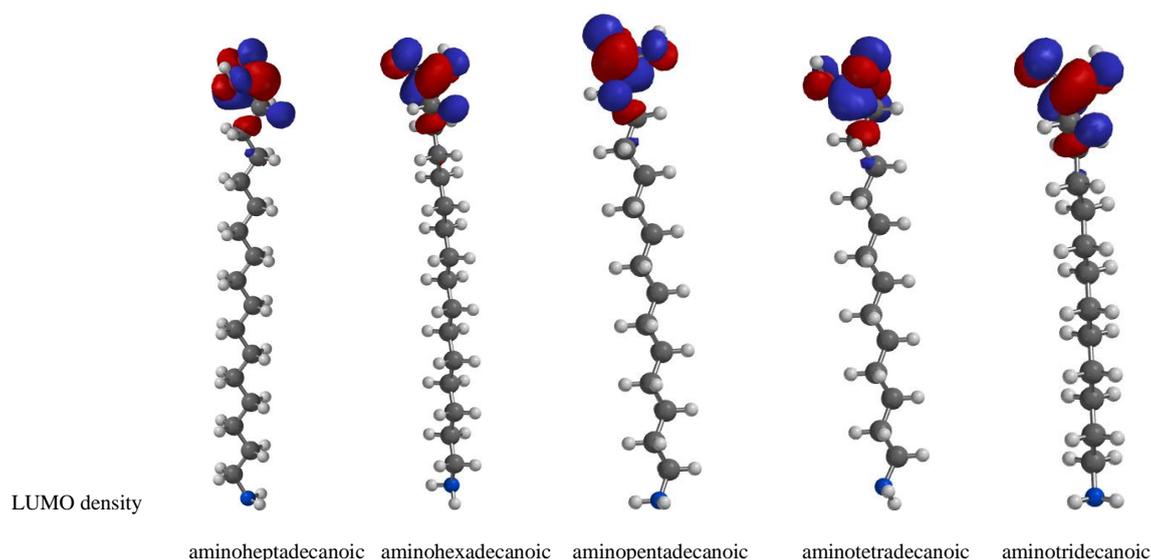
Figure 1. Optimized geometries of the studied amino acid derivatives.

Table 1. Selected molecular properties of the neutral and the protonated species for the studied amino acids.

| Structures	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{H-L} (eV)	μ (Debye)	hardness (η)	softness (σ)	(ΔN)
neutral species							
aminoheptadecanoic acid	−6.19	0.29	6.48	1.74	3.24	0.309	0.46
aminohexadecanoic acid	−6.23	0.30	6.53	1.59	3.27	0.306	0.45
aminopentadecanoic acid	−6.19	0.29	6.48	1.72	3.24	0.309	0.46
aminotetradecanoic acid	−6.23	0.30	6.53	1.72	3.27	0.306	0.45
aminotridecanoic acid	−6.20	0.29	6.49	1.70	3.25	0.308	0.46
protonated species							
aminoheptadecanoic acid	−7.03	−6.88	0.15	44.86	0.08	13.333	46.37
aminohexadecanoic acid	−7.08	−6.92	0.16	41.62	0.08	12.500	43.75
aminopentadecanoic acid							
aminotetradecanoic acid	−7.13	−6.95	0.18	36.06	0.09	11.111	39.11
aminotridecanoic acid	−7.25	−6.94	0.31	33.87	0.16	6.452	22.89

The electronic parameters related to the reactivity of the amino acid derivatives are reported in table 1 and they include, the HOMO energy (E_{HOMO}), the LUMO energy (E_{LUMO}), the energy difference between the HOMO and the LUMO orbitals (E_{H-L}), the dipole moment, global hardness and softness and the optimum number of electrons that can be donated by the inhibitor molecule. E_{HOMO} indicates the tendency of the molecule to donate electrons, with the trend often being that the higher E_{HOMO} is, the greater is the ability of that molecule to donate electrons. Among the studied amino

derivatives, aminoheptadecanoic acid and aminopentadecanoic acid have the highest E_{HOMO} while aminohexadecanoic acid and aminotetradecanoic acid have the lowest E_{HOMO}.

E_{LUMO} indicates the tendency of the molecule to accept electrons, with the trend often being that the lower E_{LUMO} is, the greater is the ability of that molecule to accept electrons. The amino derivatives investigated in this work demonstrate similar E_{LUMO}, with the difference in E_{LUMO} not exceeding 0.01eV. The energy difference between HOMO and LUMO orbitals indicates the trend towards reactivity. A high E_{H-L} is associated with a less tendency towards reactivity while a low E_{H-L} is an indication of a great tendency towards reactivity. The results of the study suggests that aminoheptadecanoic acid and aminopentadecanoic acid have the highest tendency to reactivity; this is not surprising considering that these compounds also have the highest tendency towards electron donation.

The reactivity of corrosion inhibitors may also be discussed in terms of chemical hardness and softness parameters. These quantities are often associated with the Lewis theory of acid and bases and Pearson's hard and soft acids and bases [25]; a hard molecule has a large ΔE and therefore is less reactive; a soft molecule has a small ΔE and is therefore more reactive. Adsorption occurs most probably at the region of the molecule where σ has the highest value [26]. In the study of corrosion inhibitors and their ability to bind on the metal surface, the inhibitor is considered as a soft base and the metal surface as a soft acid. The values of σ reported in table 1 show that aminoheptadecanoic acid and aminopentadecanoic acid have the smallest value.

The number of transferred electrons (ΔN) is also an indication of the ability of the molecule to donate electrons and therefore to bind on the metal surface. Although this is a calculated value (and therefore it does not represent the actual number of electrons transferred during an electrochemical reaction), it serves to give a rough estimation of the possible trend in the electron transfer among selected molecules. The compound that has the highest ability to transfer electrons is considered to have the highest tendency to interact with the metal surface. The results of the study on the amino acid derivatives, indicates that aminoheptadecanoic acid and aminopentadecanoic acid have the highest tendency to transfer electron to the metal surface.


aminoheptadecanoic acid

aminohexadecanoic acid
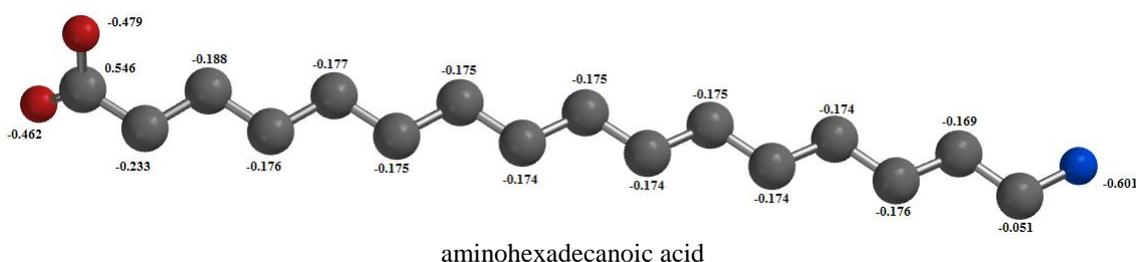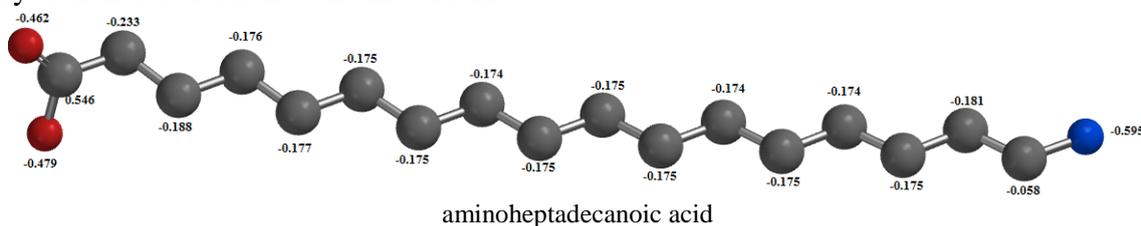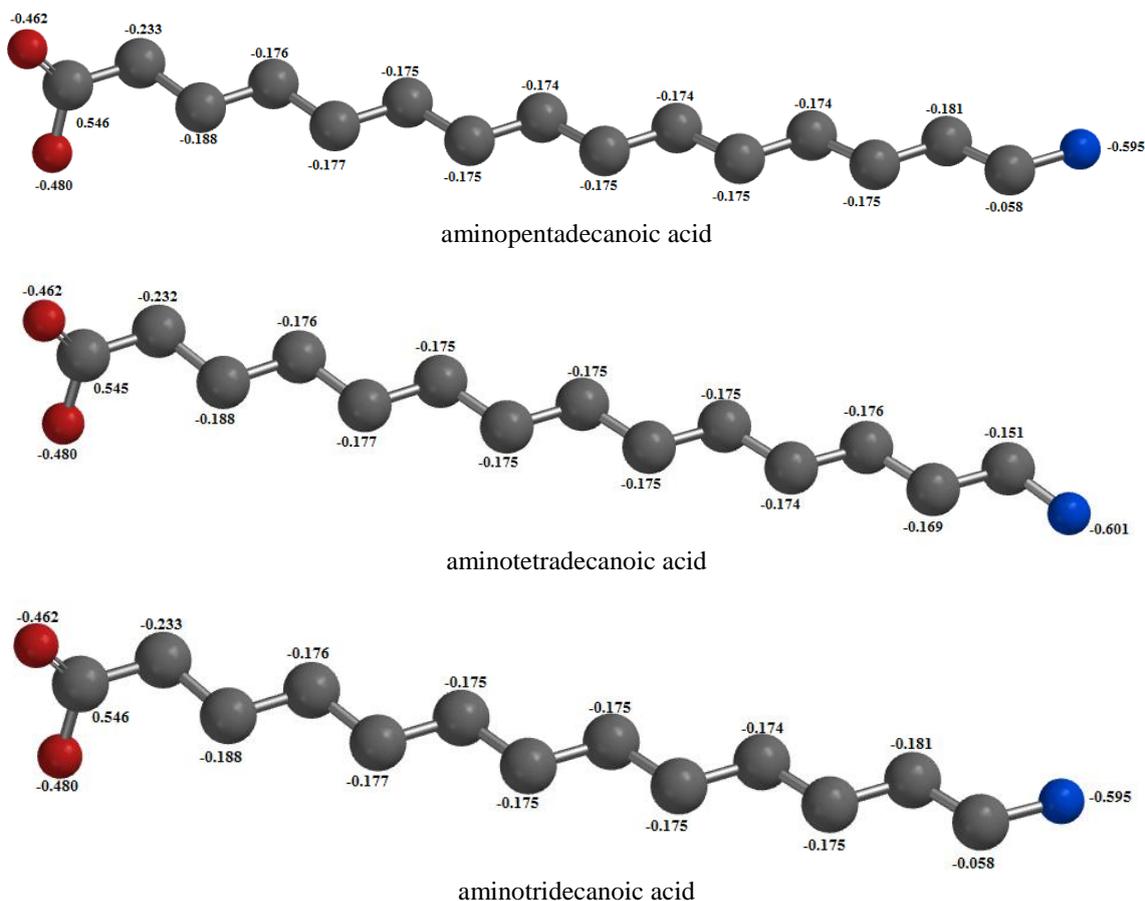
Figure 2. Mulliken atomic charges on the neutral species of the studied Amino acid derivatives. Only the heavy (non-hydrogen) atoms are shown

The partial atomic charges on the atoms of the inhibitor molecules provide information on the selectivity of the molecules on interaction with metal surface. The atoms with the highest negative charge are considered to have the highest tendency to donate electrons to the metal surface. Therefore, the inhibitor is likely to interact with the metal surface through such atoms. The charge on the heavy atoms of the studied amino acid derivatives is shown in figure 2. The results suggest that the N atom has the highest negative charge for all the atoms. This indicates that the amino group is the most likely site for the inhibitor to donate electron to the metal surface

The local selectivity of an inhibitor (i.e., the site on the molecule at which a particular reaction is likely to occur) may also be analyzed using the condensed Fukui functions. These functions (indices) provide information about which atoms in a molecule have a higher tendency to either donate or accept an electron or pair of electrons. The nucleophilic and electrophilic Fukui functions can be calculated using the finite difference approximation, which when reduced to Mulliken atomic charges is written as [27]

$$f^{+} = q_{(N+1)} - q_{N} \qquad (6)$$

$$f^{-} = q_{N} - q_{(N-1)} \qquad (7)$$

where $q_{(N+1)}$, q and $q_{(N-1)}$ are the charges of the atoms on the systems with N+1, N and N–1 electrons respectively. The preferred site for nucleophilic attack is the atom or region in the molecule

where the value of f^+ is the highest while the preferred site for electrophilic attack is the atom/region in the molecule where the value of f^- is the highest. The calculated Fukui functions on the heteroatoms, in the amino acid derivatives, are reported in table 2.

Table 2. Fukui condensed functions estimated from Mullike atomic charges of the atoms. The letters f^+ and f^- represent respective regions on the molecule at which nucleophilic and electrophilic attack is likely to occur.

Structures	f^+			f^-		
	O sp^2	O sp^3	N	O sp^2	O sp^3	N
aminoheptadecanoic acid	-0.131	-0.060	0.035	-0.096	-0.030	-0.148
aminohexadecanoic acid	-0.134	-0.061	0.045	-0.107	-0.034	-0.153
aminopentadecanoic acid	-0.134	-0.060	0.038	-0.102	-0.033	-0.154
aminotetradecanoic acid	-0.138	-0.062	0.049	-0.115	-0.037	-0.160
aminotridecanoic acid	-0.139	-0.062	0.043	-0.109	-0.035	-0.162

The value of f^+ is highest on the O sp^2 atom. This atom, therefore, represents the preferred sites for nucleophilic attack. The values of f^- is highest on N atom and therefore this atom represents regions on the molecules for which there is a high preference for an electrophilic attack. The information obtained from the Fukui condensed functions agrees with the analysis of the HOMO/LUMO and the Mulliken atomic charges, that the amino group has the highest tendency to donate electrons and the region with the highest tendency to accept electrons is the carboxylic acid group.

3.2 Results of the study on the protonated species

The presence of heteroatoms in the molecules of amino acid derivatives suggests high tendency towards protonation in acidic solution. Therefore it is important to investigate the protonated forms of the studied structures in order to determine the preferred form of the amino acid to interact with the metal surface in acid solution. The extent of protonation is provided by the proton affinity of the inhibitors which is estimated using the equation

$$PA = E_{prot} + E_{H2O} - E_{non-prot} - E_{H3O}^+ \tag{8}$$

where E_{prot} and $E_{non-prot}$ are the total energies of the protonated and the non-protonated inhibitors respectively, E_{H2O} is the total energy of a water molecule and E_{H3O+} is the total energy of the hydronium ion. The most interesting site for protonation on the amino derivatives is the sp^2 O atom. Upon protonation on this atom, the proton affinity energy is -27.458 kcal/mol for aminoheptadecanoic acid, -27.749 kcal/mol for aminohexadecanoic acid, -27.711kcal/mol for aminotetradecanoic acid and -27.390 kcal/mol for aminotridecanoic acid. The proton affinity values show that the protonation is downhill exothermic and that it is similar across structures.

A comparison of the molecular properties between the protonated and the non-protonated species of the individual structures shows that the protonated form has the lowest E_{HOMO}, what

suggests that protonation decreases the tendency of an inhibitor to donate electrons. This phenomenon may be explained as follows; the protonation of a molecule results in an increased nuclear charge so that the nuclear charge pulls more strongly on the outer electrons. As a result the ionization energy (i.e., the energy required to remove an electron) is higher in the protonated species than in the non-protonated species. Since the energy of the HOMO is related to the ionization energy (IE) through the equation $E_{HOMO} = -IE$, an increase in the ionization energy implies a lower E_{HOMO} value. The E_{LUMO} value is lowest for protonated species, what suggests that protonation increases the tendency of an inhibitor to accept electrons. The protonated species also has the smallest ΔE value, indicating that for each structure the protonated species is the most reactive form. The protonated form also has the lowest hardness and the highest softness values.

### 3.3. Adsorption mechanism on the metal surface: A molecular dynamic study

All the selected compounds have similar functional groups (i.e., the long alkyl group, the carboxylic acid group and the amino group). It is therefore reasonable to consider that their mode of interaction with the metal surface would be similar. Therefore, it was considered that the study of the aminotridecanoic acid (ATDA, i.e., the structure with the shortest alkyl chain) would provide sufficient representative information for the rest of the compounds.

The different geometries obtained on different surfaces and in different media are shown in figure 3. The study on Fe(110) surface indicates that the binding energy between ATDA and the metal surface is smallest *in vacuo*. In water solution, the binding energy increases nearly 6 times with respect *to vacuo*. This increase the binding energy is the manifestation of the stabilizing role of the solvent molecules. In the presence of hydrosulphuric acid (H_2S) the binding energy increases by is -81.663 kcal/mol with respect to the results in pure water solution. The highest binding energy is obtained in hydrochloric acid, indicating that the binding strength of ATDA increases with the increase in the acid strength. All the interaction energies (in different media) are negative values, indicating that the interaction between the Fe (110) surface and ATDA involve exothermic reactions.

a) Fe(100)···ATDA interactions in different media
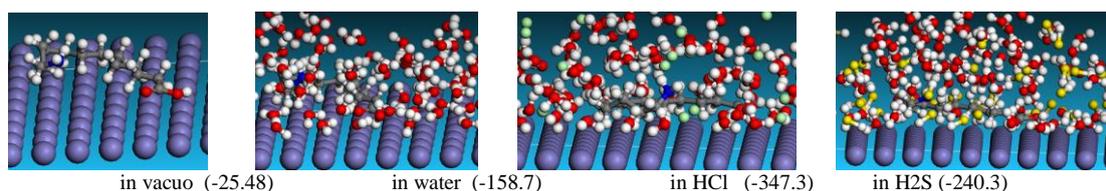
in vacuo (-25.48)   in water (-158.7)   in HCl (-347.3)   in H2S (-240.3)

b) FeCO3(100)···ATDA interactions in different media

in vacuo (-8237.5)   in water (-8158.7)   in HCl (-6820.7)   in H_2S (-7938.1)

c) FeS$_2$(100)···ATDA interactions in different media

| in vacuo (153.2) | in water (-26.1) | in HCl (-45.9) | in H$_2$S (-64.7) |

d) Fe$_2$O$_3$(100)···ATDA interactions in different media

| in vacuo (156.1) | in water (406.4) | in HCl (409.6) | in H$_2$S (491.4) |
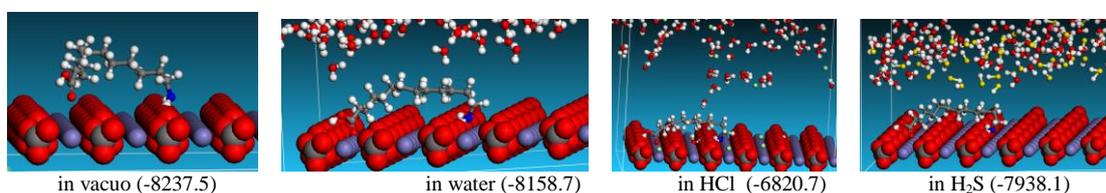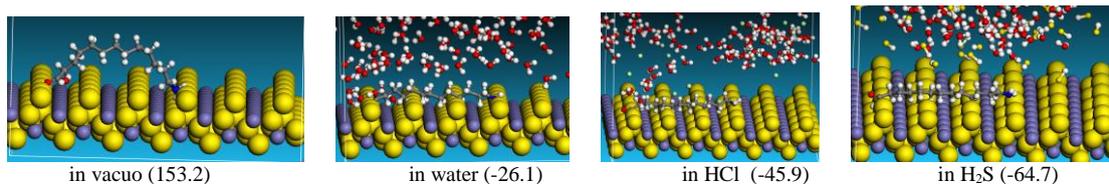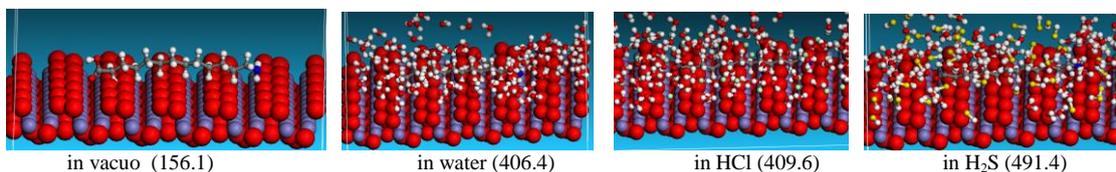
Figure 3. Geometries of molecular surface interactions, showing the ATDA molecule binding on different metal surfaces and in different media. The interaction energies (kcal/mol) are given in brackets below each structure.

The study on FeCO$_3$(110) surface indicates that the binding energy between ATDA and the metal surface is smallest in the hydrochloric acid medium and largest *in vacuo*. The binding energies therefore suggest that ATDA bind less on the metal surface when it is in acidic medium than when it is in non-acidic medium. The geometry of the FeCO$_3$(110)···ATDA *in vacuo* shows that ATDA binds to the surface by forming intermolecular hydrogen bonds (through the sp^2 O atom of the COOH and the H atoms of the NH$_2$ group). The shortest distance between the O atoms on the metal surface and the H atoms of the NH$_2$ group is 1.599Å and 1.866 Å, which indicates strong hydrogen bonding. The shortest distance between the Fe atom and the sp^2 O atom of the COOH is 3.425 Å. In water solution, the distance between the sp^2 O atom of the COOH and the nearest Fe ion is 2.200 Å; the distance between the H atom of the COOH and the nearest O atom of the FeCO$_3$(110) surface is 1.327 Å; the distance between the H atoms of the NH$_2$ group and the nearest O atoms of the FeCO$_3$(110) surface is 1.824Å and 1.829 Å; the distance between the N atom of the NH$_2$ group and the nearest Fe atom is 2.089 Å. All these geometry parameters indicate strong interactions between the metal surface and ATDA. In hydrochloric acid, the geometry of FeCO$_3$(110)···ATDA is similar to that obtained in pure water. The results also show that the water molecules as well as some Cl anions bind to the metal surface

In comparison to the results obtained on the Fe(110) surface, ATDA binds more strongly on the FeCO$_3$ (110) surface than on the Fe(110) surface. All the interaction energies (in different media) are also negative values, indicating that the interaction between the FeCO$_3$ (110) surface and ATDA would probably involve exothermic reactions.

The study on FeS$_2$ (110) surface indicates that the interaction energy *in vacuo* has a positive value, suggesting that ATDA has minimal tendency to bind to the metal surface. ATDA interact with the FeS$_2$ (110) surface through the sp^2 O atom and the CH$_2$NH$_2$ group; the distance between the sp^2 O atom and the nearest S atom is 2.903Å. In all other media, the interaction energy has negative values suggesting that the reaction in water solution, in hydrosulphuric acid and in hydrochloric acid involve

exothemic reactions. The geometry of FeS$_2$ (110)···ATDA in water, in hydrosulphuric acid and in hydrochloric acid solution clearly shows that ATDA bind to the FeS$_2$ (110) surface through the COOH group, the alkyl CH$_2$ groups and the NH$_2$ group, which may account for the high binding energy as compared to the outcome *in vacuo*. The bind energy values suggest that reaction in a less acidic media (H$_2$S) is preferred to the reaction in a more acidic media (HCl). The binding energy obtained on the FeS$_2$ (110) surface is the smallest in comparison to the Fe (110) and FeCO$_3$ (110) surfaces.

The study on Fe$_2$O$_3$ (110) surface indicates that the interaction energies in all the media have positive values. This result suggest that ATDA has less tendency to interact with the Fe$_2$O$_3$ (110) surface, especially in acidic media. The geometry of the Fe$_2$O$_3$ (110)···ATDA (figure 3) suggests that ATDA interacts with the surface through its sp^2 O atom, the CH$_2$ groups of the long alkyl chain and the H atoms of the NH$_2$ group. The distance between the metal surface atoms and the C atoms of the alkyl chain has a range of 2.895–3.255Å. The O atoms on the metal surface are more in contact with ATDA than the Fe atoms, which increase the repulsion between the lone pair of electrons on the O atoms on the Fe$_2$O$_3$ (110) surface and the lone pair of electrons on the sp^2 O atom. The resulting repulsion may explain the fact that the ATDA has less tendency to bind to the Fe$_2$O$_3$ (110) surface. The results obtained here is a consequence of the fact that there is non-homogenous arrangement of O and Fe ions on the Fe$_2$O$_3$ (110) surface, with more O atoms on the surface. The situation may however be very different in an actual Fe$_2$O$_3$ (110) surface.

4. CONCLUSION

Theoretical studies have been performed on selected amino acid derivatives to investigate their ability to bind on the metal surface. DFT studies were performed to determine and compare their molecular properties and molecular dynamics studies were performed to investigate their binding properties on different metal surfaces and in different media. The results of the study suggest that all the compounds have high tendency to interact with metal surfaces. All electronic parameters indicate the high tendency of aminoheptadecanoic acid and aminopentadecanoic acid to interact with the metal surface through the amino group and the carboxylic acid group. The study on different metal surface however show that the binding energy of the molecule on different surfaces follow the order Fe$_2$O$_3$ < FeS$_2$ < Fe(110) < FeCO$_3$.

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