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A DFT and Molecular Dynamics Study on Inhibitory Action of Three Amine Derivatives on Corrosion of Carbon Steel

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Abstract

Inhibition efficiencies of three amine derivatives (Diethylenetriamine (I), Triethylenetetramine (II), and Pentaethylenehexamine (III)) have been studied on corrosion of carbon steel using density functional theory (DFT) method in gas phase. Quantum chemical parameters such as EHOMO (highest occupied molecular orbital energy), ELUMO (lowest unoccupied molecular orbital energy), hardness (η), polarizability (α), dipole moment (μ), electrophilicityindex (ω) totalnegative charges on atoms (TNC) and molecular volume (MV) have been calculated at the B3LYP level of theory with 6-311++G ** basis set. Moreover, adsorption behavior of the inhibitor molecules on Fe (110) surface has been analyzed using molecular dynamics simulation. The binding strength of the concerned inhibitor molecules on Fe (110) surface follows the order III>II>I, which is in good agreement with the experimentally determined inhibition efficiencies. In consistent with experimental data, theoretical results showed that the order of inhibition efficiency is Pentaethylenehexamine (III)>Triethylenetetramine (II)>Diethylenetriamine (I). This study has shown that DFT along with MD can be successfully be used as a reliable approach to screen organic corrosion inhibitors prior to experimental validation.

Key words: *Corrosion, Inhibition efficiencies, Quantum Chemical Parameters, Molecular Dynamics Simulation, Carbon Steel.*

Introduction

Corrosion is defined as the degradation of a metal either by direct chemical or electrochemical reaction in contact with aqueous corrosive surroundings [1, 2]. Corrosion of mild steel is a major concern for a long time due to frequent use of mild steels in various industrial divisions. The

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protection of metal surfaces against corrosion is an important industrial and scientific topic. Several classes of organic compounds are widely used as corrosion inhibitors for metals in acid environments [3]. Evaluation of corrosion inhibitors for mild steel is important for both theoretical and industrial point of views for the last decades; quantum chemistry has become an effective way in studying the relationship between the inhibitor molecular properties and structure with inhibition efficiencies.

In the Quantum chemical methods, several factors and quantum chemical parameters are checked to study the corrosion inhibitive potentials of inhibitors. From the 1970s, successful research has been carried out in the field of corrosion inhibition using different computational approaches [4-8]. However, quantum chemistry computing methods are computationally expensive and are usually only applied to systems containing no more than 100 atoms or small molecules. It is not practical to model large systems containing dozens of metal atoms and hundreds of solvent molecules. Molecular dynamics (MD) simulation has been another effective tool often used to study the interaction of inhibitors with the metal surface [9-12].

Migahed et al. [13] have recently reported experimentally inhibition efficiencies of some amine derivatives for carbon steel corrosion in cooling water systems. Herein, inhibition effects of three amine derivatives(**Fig. 1**) have been investigated on corrosion of carbon steel using some quantum chemical parameters such as EHOMO (highest occupied molecular orbital energy), ELUMO (lowest unoccupied molecular orbital energy), hardness (η), polarizability (α), total negative charges on atoms (TNC), molecular volume (MV), dipole moment (μ) and electrophilicity (ω). This study displays a good correlation between the theoretical and experimental data which confirms the reliability of the quantum chemical methods for studying the inhibition of corrosion of metal surfaces.

Also, Molecular dynamics simulation which has been proven to be efficient in the evaluation of the interaction of organic compounds with metal, was used to analyze the adsorption energies of amine compounds upon the Fe (110) surface.

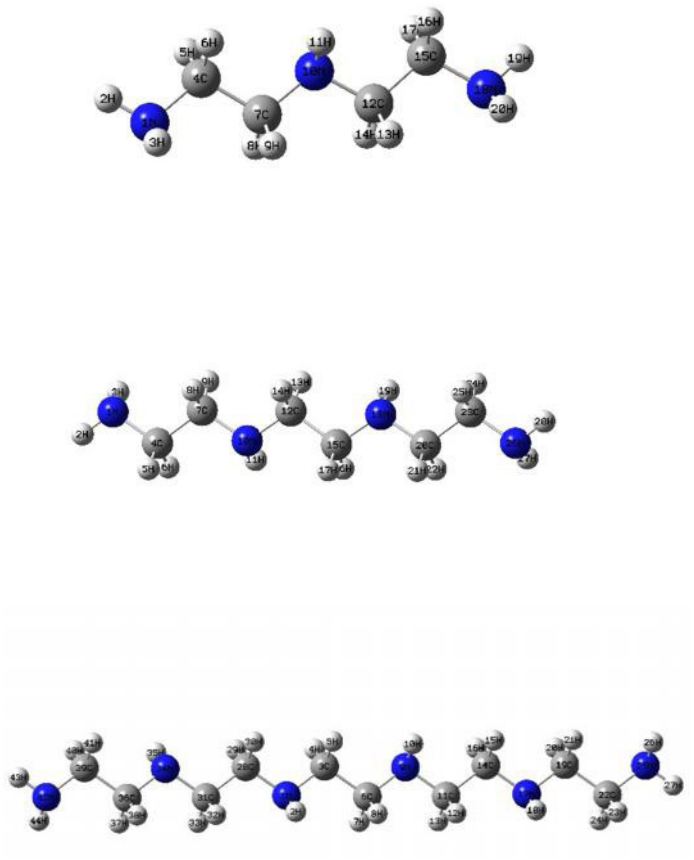

Figure 1. Optimized structures of studied amines.

Quantum chemical calculations and dynamic simulations

Quantum chemical calculations were performed for three amines as corrosion inhibitors using the density functional theory (DFT) method at the hybrid functional B3LYP level of theory with

6-311++G** basis set [14-16] by the Gaussian 03 series of programs [17]. Frequency calculations were also carried out on optimized geometries to find out the nature of the stationary point on the potential energy surface. The theoretical parameters were calculated in gas phase.

Molecular properties, in relation to the reactivity of the compounds, were estimated following the Koopmans's theorem relating the energy of the HOMO (E_H) and the LUMO (E_L) [18].

Global hardness (η) measures the resistance of an atom to a charge transfer [19]; it is calculated using the equation (1):

$$\eta = \frac{1}{2}(E_L - E_H) \qquad (1)$$

Electronegativity χ is the measure of the power of an atom or group of atoms to attract electrons to it when chemically combined with another atom [20], it can be expressed with the equation (2):

$$\chi = -\frac{1}{2}(E_L + E_H) \qquad (2)$$

Global electrophilicity index (*ω*), has been proposed by Parr et al is the measure of the electrophilic tendency of a molecule [21]; it is can be obtained from the definitions of global hardness and the electronegativity as follows:

$$\omega = \frac{\chi^2}{2\eta} \qquad (3)$$

This was proposed as a measure of the electrophilic power of a molecule. A good nucleophile is characterized by low value of *ω*; while a good electrophile is characterized by high value *ω* [22]. The higher value ofω, the higher capacity of the molecule to accept electrons. During the interaction of the inhibitor molecule with bulk metal, electrons flow from the lower electronegativity molecule to the higher electronegativity metal until the chemical potential becomes equalized. The fraction of the transferred electron, ΔN, was stated through the equation (4):

$$\Delta N = \frac{\chi_m - \chi_i}{2(\eta_m + \eta_i)} \qquad (4)$$

Where the indices "m" and "i" refer to metal atom and inhibitor molecule, respectively and where χ_m and χ_i represent the absolute electronegativity of iron and the inhibitor molecule, respectively; η_m and η_i state the absolute hardness of iron and the inhibitor molecule, respectively. The theoretical values of χ_m and η_m were employed 7 eV.mol^{-1} and 0 eV.mol-1 for bulk iron, respectively by means of an approximation for a metallic bulk I = A, because they are softer than the neutral metallic atoms [23, 24].

Actually, the value of 7.0 eV corresponds to the free electron gas Fermi energy of iron in the free electron gas model. Where the electron–electron interaction is neglected, and the use of this value as χ_{mis} conceptually wrong [25, 26]. Therefore, some researchers demonstrated that the work functions (φ_m) of a metal surface is an appropriate measure of its electronegativity and should be used in the estimation of ΔN[27, 28] , as follows:

$$\Delta N = \frac{\varphi_m - \chi_i}{2(\eta_m + \eta_i)} \qquad (5)$$

The surface energy of Fe planes is, typical for bcc transition metals, in the order of E(110) < E(100) < E(111) [29], thus the most stable plane would be Fe(110). Herein, in this study we had chosen Fe (1 1 0) surface among other optional Fe surfaces. Where the φ_m value obtained from DFT calculations is 4.82 eV for Fe (110) surfaces [30]. The electric dipole polarizability (*α*) is a measurement of the linear response of the electron density in the presence of an infinitesimal electric field F and it descript a second order variation in energy:

$$\alpha = -\left(\frac{\partial^2 E}{\partial^2 F_a\, \partial^2 F_b}\right) \qquad a,b= x, y, z \qquad (6)$$

The polarizability (α) is calculated as the mean value and express through the equation (7):

$$\alpha = \frac{1}{3}\left(\alpha_x + \alpha_y + \alpha_z\right) \qquad (7)$$

It was discovered that polarizabilities are inversely proportional to the third power of the hardness values [31, 32]. On the basis of this fact, the minimum polarizability principle (MPP) has been suggested [33], with respect to this point, 'the natural direction of evolution of any system is towards a state of minimum polarizability'. This principle is also applied for chemical reactions and it is deduced that in chemical reactions, the most stable species (reactants or products) have the lowest sum of $\alpha^{\frac{1}{3}}$ [34]. A theoretical proof of such a principle does not exist. Molecular dynamics simulation (MD simulation) is a technique which is popular to studies of interaction between inhibitor and the concerned metal surfaces. The interaction between an inhibitor and iron (Fe) surface is investigated by MD simulation using the Forcite module of the Materials Studio 6.0 software developed by Accelrys Inc [35]. As earlier observed for Fe [29], the most stable plane would be Fe(110). Herein, in this study we had chosen Fe (1 1 0) surface among other optional Fe surfaces for simulation.

The interaction between Fe (110) surface and inhibitor molecules is carried out in a simulation box (37.23×37.23×72.11Å) with periodic boundary conditions. A vacuums lab of 50Å height is kept over the Fe (110) surface. Non-bonding, van der Waals and electrostatic interactions were set as atom-based summations using the Ewald summation method with a cutoff radius of 15.50Å.Using twenty layers of iron atoms gives a sufficient depth that the inhibitor molecules will only be involved in non-bond interactions with iron atoms in the layers of the surface, without unreasonably increasing the calculation time. During the simulation process all the atoms in the Fe (110) surface were fixed and inhibitors are allowed to interact with the metal surface freely. The interaction of inhibitors on the Fe (110) surface is then simulated by COMPASS force field. The MD simulation is performed at 298.0 K under canonical ensemble (NVT) using a time step of 1.0 f s and a simulation time of 100 ps. the geometry of the system was optimized such that the total energy of the system was at a local minimum with respect to potential energy. Then, the dynamic process was carried out until the entire system reached equilibrium, at which both the temperature and the energy of the system were balanced.

The interaction energy between the metal and the inhibitors was then considered as the difference between when the adsorption occurs between the surface and adsorbed inhibitor molecule, the energy of the new system is expressed as ($E_{Fe\text{-}X}$) and the sum of the total energy of the surface without the inhibitor and the energy of the inhibitor without the surface. ($E_X + E_{Fe}$) resulted in the equation[35];

$$E_{int} = E_{(Fe.\text{-}X)} - (E_X + E_{Fe}) \qquad (8)$$

Result and discussion

The global molecular reactivity was investigated via analysis of the frontier molecular orbitals (FMO) in terms of interaction between the frontier orbitals, involving the HOMO and the LUMO [36]. EHOMO describes the electron donating ability of the molecule. Therefore, inhibitors with high values of EHOMO have a tendency to donate electrons to an appropriate acceptor with a low empty molecular orbital energy. On the other hand, the energy of LUMO indicates the ability of the molecule to accept electrons. The lower value of E_{LUMO}, the more probable it is that the molecule accepts electrons.

The inhibition efficiency increases with the enhancement of E_{HOMO} values. High E_{HOMO} values indicate that the molecule has a tendency to donate electrons to the appropriate acceptor molecules with a low-energy empty molecular orbital. The lower value of E_{LUMO} suggests the molecule easily accepts electrons from the donor molecules [37]. Table 1 presents the calculated values of E_{HOMO} and E_{LUMO} for the studied three amine in gas phase. Based on the increasing value of E_{HOMO}, the order for the variation of inhibition efficiencies of the studied inhibitors is consistent with the order obtained from experimental data (III > II > I)[13]. The trend obtained for E_{LUMO}, is compatible well with the trend in the experimentally determined inhibition efficiency.

Absolute hardness is a very significant parameter when discussing molecular reactivity and stability. Soft molecules indicate more reactivity than hard ones because they can donate electrons without difficulty. Hence, inhibitors with the least values of global hardness are expected to be well corrosion inhibitors for bulk metals. On the basis of Wang et al. investigation[38], adsorption of inhibitor onto a metallic surface occurs at the part of the molecule which has the greatest softness and lowest hardness. Moreover, Table 1 present the calculated values of η for the chosen amines in gas phase. The results exhibit that III and II have the least hardness values compared to I, respectively.

Table 1. Quantum chemical parameters of the studied amines in gas phase calculated at B3LYP/6311++G** level.

		E_{HOMO} (ev)	**E_{LUMO} (ev)**	**η (ev)**	**χ (ev)**	**ΔN (e)**	**α (a.u.)**	**MV (cm^3/mol)**	**μ (Debye)**	**ω (ev)**	**TNC (e)**
gas	III	-6.12	-0.438	2.84	3.281	0.270	185.8	228.1	3.510	1.894	-6.13
	II	-6.15	-0.414	2.86	3.282	0.268	115.4	136.7	3.340	1.878	-4.08
	I	-6.20	-0.390	2.90	3.301	0.261	80.3	107.8	2.930	1.877	-3.07

The electronegativity expresses the tendency of an atom in a molecule to attract electrons toward it. Since good inhibitors are usually those which are capable of donating electrons to the metallic surface, so we are expected that the electronegativity values will decrease with the enhancement of inhibitive efficiencies. In addition, the values of χ for the present system are accumulated in Table 1. The trend in the χ values for the mentioned inhibitors show III has the lowest value of electronegativity. This effect increases its adsorption on the mild steel surface and therefore enhances its corrosion inhibition efficiency when compared to II and I, respectively.

The calculated electrophilicity values for each one inhibitor are included in Table 1. Data in Table 1shows that the electrophilicity index of the inhibitor molecules follow the trend: III >II> I. The calculated high value of electrophilicity index (ω) for III shows that this molecule behaves as a strong electrophile than II and I which confirms its high capacity to accept electrons. Thus, unoccupied d orbitals of Fe atom can accept electrons from inhibitor molecule to form a coordinate bond. Also the inhibitor molecule can accept electrons from Fe atom with its anti-bonding orbitals to form back-donating bond. These donation and back-donation processes strengthen the adsorption of III onto the mild steel surface.

The number of electrons transferred (ΔN) for species were also calculated and tabulated in Table 1. The positive number of electrons transferred (ΔN) exhibits that the molecules operate as an electron donor, while a negative number of electrons transferred (ΔN) indicates that the molecules have activity as electron acceptors[39]. Thus all the species in the current system act as electron donors. In the case of corrosion inhibitors, a higher ΔN implies a very large tendency to interact with the metal surface (i.e., a greater tendency to adsorb on the metal surface). Values of ΔN for species show that III has the highest ΔN value. As can be seen, ΔN values are strongly compatible with experimental inhibition efficiencies. Thus, the highest fraction of electrons transferred is closely associated with the best inhibitor (III), while the least fraction is connected with the inhibitor that has the least inhibition efficiency (I).

Polarizability (α) is the ability for a molecule to be polarized and this is well reactivity indicators [34]. The higher values of the polarizability facilitate the strong adsorption process of corrosion inhibitors onto metal surface and hence, high inhibition efficiency. Polarizability is the ratio of induced dipole moment to the intensity of the electric field. The induced dipole moment is proportional to polarizability [37]. Some struggles have been made to connect the polarizability of corrosion inhibitors to their inhibition efficiency. The polarizabilities were evaluated using Eq. (7) and reported in Table 1 for three amines. As can be seen, the trend for the variation of polarizability follows: III >II>I. These data reveal that the trend of increasing inhibition efficiencies of the inhibitors with respect to enhancement of polarizability is consistent well with the order of the experimental % inhibition efficiencies results (III>II>I).

The dipole moment (μ) is another important electronic parameter that results from non-uniform distribution of charges on the various atoms in the molecule. The energy of the deformability increases with the increase in μ, making the molecule easier to adsorb at the Fe surface. The high value of dipolemoment probably enhances the adsorption on the metal surface[40], In the current work, the results seemingly support this viewpoint, III has a higher value of the dipole moment than II and I.Molecular volume (MV) illustrates possible metal surface coverage by the inhibitor. The compound that has large MV value has the highest surface coverage and hence might give a very large protection to the metal surface. The inhibition efficiency speeds up as the volume of the molecules increases due to the enhancement of the contact area between the molecule and the surface. A comparison of the MV values across structures emphasize the order III > II > I. The trend in the MV values is compatible well with the experimentally determined inhibition efficiencies.The active sites of the inhibitor molecule can be determined by accounting natural atomic charge.

It is proven that charges are important in many different types of chemical reactions and the physical as well as chemical properties of compound [4]. The partial charges on the individual atoms in a molecule also indicate the reactive centers for a particular inhibitor. The atoms with the highest negative charge are considered to have the highest tendency to donate electrons to the metal surface. Thus, the inhibitor is likely to interact with the metal surface through such atoms. For this purpose, natural bond orbital (NBO) analysis was performed. Net atomic charges have been obtained using the natural population analysis (NPA). The atomic charges on the atoms of the chosen amines in gas phase are summarized in Table 2. The most favorable sites for the interaction with the metal surface for species were N heteroatoms; because these atoms have a larger negative charge, which suggests that those active centers with excess charges could act as a nucleophilic group. The binding capability of the metal on the inhibitor depends strongly on the electronic charge of the active site [41]. Each inhibitor molecule was allowed to interact with the Fe metal at the atom that has the highest negative charge.

Another parameter that was considered is the total negative charge (TNC) that can give us valuable information about the reactive behavior of the studied inhibitors. It is obtained by summing up all the negative charges within a molecule [3, 42]. Summation of the total negative charges on atoms over the skeleton of the molecule (TNC) is collected in Table 1. The calculations exhibited that the inhibitor with the highest inhibition efficiency has the highest TNC value which agrees well with the experimental observations.

As it can be seen from the atomic charges in

Table 1, the total number of charge centers (negative) was generated for the amine derivatives. The negative charge centers could donate electrons to the Fe atoms for generation of coordinate bonds while the positive charge centers can accept electrons from 3d orbitals of the Fe atom to form feedback bonds, thus further strengthening the interaction of inhibitor and Fe surface. The high inhibition efficiency of III and I can be emerged from their high number of charged centers of 16 and 10, respectively. This was confirmed by calculating TNC, where the more active sites the molecule has, the higher TNC and the higher inhibition efficiency.Many corrosion inhibition studies nowadays contain the use of molecular dynamics simulation as an important tool in understanding the interaction between adsorbate-metal surface [4, 43-45]. It has been reported that the more negative the adsorption energies, the stronger the adsorbate-metal interaction [46].

Table 2. The calculated atomic NBO (Natural bond orbital) charges (q) for selected atoms for the III, II and I inhibitorsin gas phase.

III	**q**	**II**	**q**	**I**	**q**
N 1	**-0.6755**	N 1	**-0.8458**	N 1	**-0.8457**
H 2	0.3360	H 2	0.3529	H 2	0.3527
C 3	-0.1701	H 3	0.3443	H 3	0.3443
H 4	0.1915	C 4	-0.1811	C 4	-0.1811
H 5	0.1465	H 5	0.1895	H 5	0.1892
C 6	-0.1699	H 6	0.1461	H 6	0.1457
H 7	0.1912	C 7	-0.1732	C 7	-0.1734
H 8	0.1457	H 8	0.1916	H 8	0.1917
N 9	**-0.6724**	H 9	0.1466	H 9	0.1467
H 10	0.3365	N 10	**-0.6740**	N 10	**-0.6756**
C 11	-0.1699	H 11	0.3356	H 11	0.3347
H 12	0.1455	C 12	-0.1702	C 12	-0.1734
H 13	0.1915	H 13	0.1457	H 13	0.1467
C 14	-0.1703	H 14	0.1918	H 14	0.1917
H 15	0.1462	C 15	-0.1701	C 15	-0.1810
H 16	0.1919	H 16	0.1457	H 16	0.1458
N 17	**-0.6740**	H 17	0.1918	H 17	0.1892
H 18	0.3354	N 18	**-0.6740**	N 18	**-0.8457**
C 19	-0.1732	H 19	0.3356	H 19	0.3527
H 20	0.1916	C 20	-0.1731	H 20	0.3443

H 21	0.1467	H 21	0.1916
C 22	-0.1811	H 22	0.1466
H 23	0.1459	C 23	-0.1811
H 24	0.1894	H 24	0.1461
N 25	**-0.8456**	H 25	0.1895
H 26	0.3443	N 26	**-0.8458**
H 27	0.3528	H 27	0.3443
C 28	-0.1745	H 28	0.3529
H 29	0.1883		
H 30	0.1538		
C 31	-0.1736		
H 32	0.1496		
H 33	0.1956		
N 34	**-0.6784**		
H 35	0.3445		
C 36	-0.1763		
H 37	0.1470		
H 38	0.1905		
C 39	-0.1817		
H 40	0.1466		
H 41	0.1896		
N 42	**-0.8462**		
H 43	0.3532		
H 44	0.3446		

In this study, three selected inhibitors (I, II and III) have been placed on the Fe (1 1 0) surface to find out the most favorable adsorption sites along with their suitable configuration. The best adsorption configurations for the inhibitor molecules and iron surface were depicted in Fig. 2. The calculated interaction energy obtained from molecular dynamics simulation were presented in Table 3.

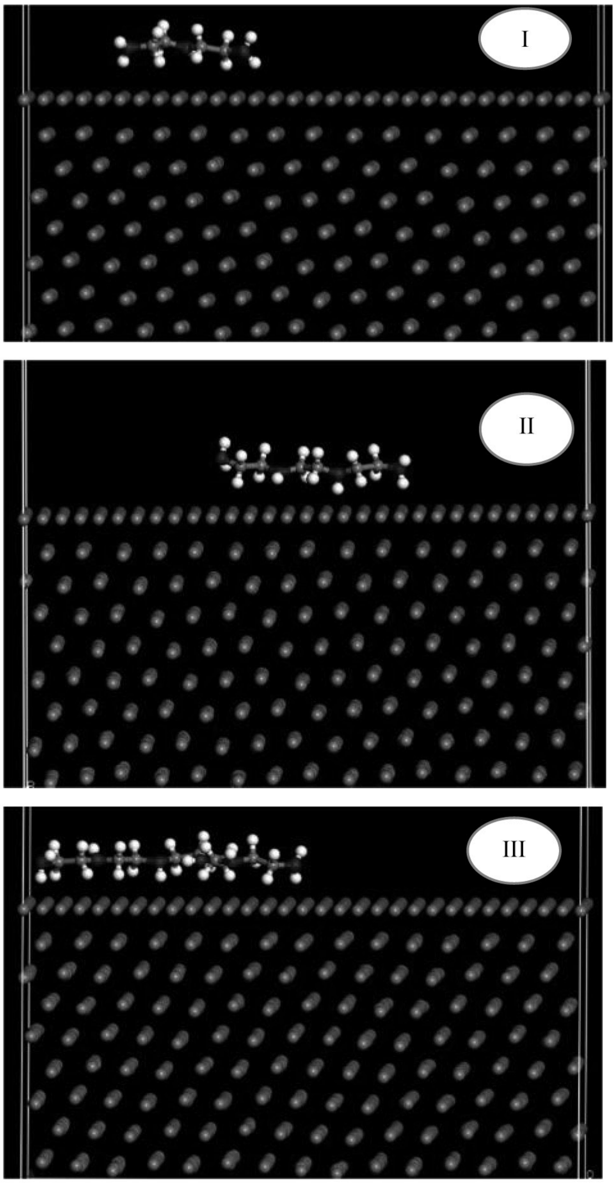

Figure 2. Equilibrium adsorption configurations of inhibitors I, II and III on Fe (1 1 0) surface obtained by molecular dynamics simulations.

Table 3. The interaction energy obtained from MD simulation for adsorption of inhibitors on Fe (1 1 0) surface.

system	$E_{interaction}$ (kcal/mol)
Fe+III	-245.589
Fe+II	-161.981
Fe+I	-110.815

As it can be seen from figure 2, inhibitor molecules have a flat or parallel orientation with respect to the iron surface. The parallel adsorption configurations ensure that the iron surface can be maximally covered by the investigated inhibitor molecules. It is evident that values of E_{int} are negative for three inhibitors implying that the adsorption on mild steel surface is spontaneous. Also, from a thermodynamic point of view, the more stable system has the lowest energy state. Therefore, we expect that the more stable formed complex has the lower values of E_{int}. It is clear from Table 3, that III gave the maximum negative adsorption energy. Therefore, III is expected to exhibit greater inhibition abilities as compared to II and I. The obtained interaction energy values have good linear correlation with inhibition efficiency. Both results (the interaction energy and the bond distances), confirm that III has a stronger adsorption on the metal surface. Accordingly, the classification of these three inhibitors based on the theoretical study is in quite a good agreement with the reported experimental corrosion inhibition efficiencies.

Conclusion

The results of DFT and MD simulations calculations on three amine derivatives (Diethylenetriamine (I), Triethylenetetramine (II), and Pentaethylenehexamine (III)) corrosion inhibitors have been presented in gas phase. Both theoretical and experimental results show that the order of inhibition efficiency is Pentaethylenehexamine (III)>Triethylenetetramine (II)>Diethylenetriamine (I). The experimental inhibition efficiencies are closely related to the quantum chemical parameters such as EHOMO, η, ELUMO, χ, TNC, MV, dipole moment (μ), electrophilicity index (ω) , α and ΔN. It is also found that the calculated molecular parameters are all in good agreement with the experimental inhibition efficiency, confirming the reliability of quantum chemical method employed herein. Quantum chemical calculations reveal that III as an inhibitor has the highest tendency to adsorb strongly onto the metal surface. Molecular dynamics simulation results reveal that interaction energy values of the three inhibitor compounds with the Fe(110)surface obey the order III > II > I, in accordance with the experimental inhibition efficiency. This study has shown that DFT along with MD can be successfully can be used as a reliable approach to screen organic corrosion inhibitors prior to experimental validation.

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