A Study on Inhibition Performance of Mercaptoalcohols As Corrosion Inhibitors by First Principle and Molecular Dynamics Simulation

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Received August 19, 2019; revised February 19, 2020; accepted March 17, 2020

Abstract—The structure–activity relationship of ten mercaptoalcohol molecules as corrosion inhibitors for carbon steel was investigated through quantum chemistry calculation and molecular dynamics simulation (MD). Quantum chemical parameters including the energy of the highest occupied molecular orbital ($E_{\text{HOMO}}$) and the lowest unoccupied molecular orbital ($E_{\text{LUMO}}$), energy gap ($\Delta E$), electronegativity ($\chi$) have been calculated to investigate the relationship between the corrosion inhibition performance and the molecular structure. Quantum chemical parameters show the corrosion inhibition performance is strengthened with the lengthening of the carbon chain. The theoretical inhibition efficiency increases with the increasing of the length of carbon chain. As a result, the C\textsubscript{11} molecule presents the best corrosion inhibition performance among the studied molecules. At the same time, molecular dynamics simulation results indicate that both the –SH and –OH can be adsorbed onto the Fe (1 1 0) surface and the molecular plane is parallel to the Fe (1 1 0) surface. The absolute values of the adsorption energy increases with the lengthening of the carbon chain. According to the adsorption energy, the longer of the carbon chain is, the easier it is for molecule to be adsorbed onto the Fe (1 1 0) surface. As a result, the corrosion inhibition performance of the mercaptoalcohol molecules becomes better with the lengthening of the carbon chain, and the C\textsubscript{11} molecule is the best one.

Keywords: corrosion inhibition performance, mercaptoalcohol, first principle, molecular dynamics simulation, structure–activity relationship

DOI: 10.1134/S0036024420090356

INTRODUCTION

Carbon steel is widely used in oil and gas industry for its relatively low cost, good machining performance. However, the harsh environment in the oil and gas field is likely to cause steel corrosion. Therefore, the study and development of corrosion inhibitor is of great significance [1–3]. Generally speaking, organic compounds containing heteroatoms (such as N, O, S, etc.) and $\pi$ electrons have good corrosion inhibition performance [4–7] by forming a protective film on the metal surface [9, 10].

Thiol as a kind of corrosion inhibitor has been studied for several decades [11, 12]. Cakir [13] proposed in his study that the inhibition performance of thiol is due to the fact that it can be adsorbed at the metal surface. He believed that the adsorption process depends upon the metal surface character, the type of aggressive environment, the molecular structure of the inhibitor, and its interaction with the metal surface. He further put forward that anions or inhibitor molecules with a negative structural moiety is more likely to be adsorbed. Chen et al. [14] have investigated the corrosion inhibition performance of dodecanethiol and determined that monolayer dodecanethiol is able to retard the reduction of dissolved oxygen and mitigate the growth of copper oxide in sodium chloride solution. Belarbi et al. [15] have studied the corrosion inhibition performance of alkanethiols. Their results show that alkanethiols are able to decrease corrosion rate when steel specimens were exposed to top of the line corrosion conditions. Belarbi et al. [16, 17] have investigated the effect of water condensation rate, monoethylene glycol, hydrogen sulfide, and hydrocarbon on the inhibition efficacy of decanethiol.

Despite numerous experimental studies on the inhibition performance of thiol, its structure–activity relationship is still not clear on the microscopic scale. Fortunately, theoretical computational chemistry provides us with an alternative. As effective methods, quantum chemical calculation and molecular dynam-
ics simulation have been widely used in studies of the corrosion inhibition performance of inhibitors [18]. These methods have been proved as useful in designing corrosion inhibitors [19, 20]. Quantum chemical studies using density functional theory (DFT) and molecular dynamics calculation have also been successfully performed by research groups to link the corrosion inhibition performance with the electronic properties of organic molecules [21–25].

Since few theoretical researches have been reported on the inhibition performance involving thiols, the objective of the present work is to bridge the gap in information using quantum chemistry calculation and molecular dynamics simulation to provide theoretical insights into the structure—activity relationship of ten mercaptoalcohol molecules and analyze the adsorption stability on carbon steel surface. The structure of the mercaptoalcohol molecules was shown below:

\[
\text{HS} \quad n = 0 - 9
\]

**CALCULATION METHODOLOGIES**

**Quantum Chemical Calculations**

In this work, DFT calculations were performed by the Gaussian 09 [26] software package. Firstly, the molecular structure was optimized with the M06-2x method combined the 6-311++G** basis set [27, 28]. And then the energy of the highest occupied molecular orbital (\(E_{\text{HOMO}}\)) and the energy of the lowest unoccupied molecular orbital (\(E_{\text{LUMO}}\)), dipole moment (\(\mu\)) were calculated at the same level based on the optimized geometry.

According to the frontier molecular orbital theory, the electron transition occurs between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [29]. So, the frontier molecular orbitals are very important for defining the reactivity [30]. Frontier molecular orbitals are able to predict the adsorption centers of the inhibitor molecule [31, 32]. According to DFT-Koopman’s theorem [33], the first vertical ionization potential (\(I\)) and the electron affinity (\(A\)) can be obtained as the negative values of the energy of the highest occupied molecular orbital (\(E_{\text{HOMO}}\)) and the energy of the lowest unoccupied molecular orbital energy (\(E_{\text{LUMO}}\)), respectively.

\[
I = -E_{\text{HOMO}}\quad (1)
\]

\[
A = -E_{\text{LUMO}}\quad (2)
\]

Natural bond orbital (NBO) analysis [34] was performed to evaluate the electron density distributions. The electron density plays an important role in calculating the chemical reactivity parameters. The global reactivities including electronegativity (\(\chi\)), global hardness (\(\eta\)), and global softness (\(\sigma\)) [35, 36] can be calculated from the following equations:

\[
\chi = \frac{I + A}{2},
\]

\[
\eta = \frac{I - A}{2},
\]

\[
\sigma = \frac{2}{I - A}. \quad (5)
\]

The electron transfer number \(\Delta N\) provides the number of electrons transferred by the corrosion inhibitor to the metal atom, and the calculation formula is as follows:

\[
\Delta N = \frac{\chi_{\text{Fe}} - \chi_{C-x}}{2(\eta_{\text{Fe}} + \eta_{C-x})}. \quad (6)
\]

Herein, \(\chi_{\text{Fe}}\) and \(\eta_{\text{Fe}}\) represent the absolute electronegativity and global hardness of the iron atom, respectively, while \(\chi_{C-x}\) and \(\eta_{C-x}\) are the corresponding parameters for the inhibitor molecules. In the above equation, two empirical constants for \(\chi_{\text{Fe}}\) and \(\eta_{\text{Fe}}\) were set as 7 and 0 eV, respectively. This is due to the assumption that \(I = A\) for a metallic bulk since they are usually softer than the neutral metallic atoms.

The local reactivity has been analyzed by means of Fukui index [37], which is an indication of the reactive centers within the molecules. These are measurements of the chemical reactivity, as well as an indicative of the reactive regions, nucleophilic and electrophilic behavior of the molecule [38]. The condensed Fukui functions were found by taking the finite difference approximations from Mulliken population analysis of atoms in inhibitor molecules, depending on the direction of the electron transfer. With this approximation, one can derive the condensed Fukui functions for an electrophilic active site (\(f_\ast^+\)) and a nucleophilic active site (\(f_\ast^-\)):

\[
f_\ast^+ = q_k(N + 1) - q_k(N), \quad (7)
\]

\[
f_\ast^- = q_k(N) - q_k(N - 1), \quad (8)
\]

where \(q_k(N)\), \(q_k(N + 1)\), and \(q_k(N - 1)\) are the electronic population of the atom \(k\) in neutral, cationic and anionic systems, respectively [39].

**Molecular Dynamics Simulations**

In this paper, molecular mechanics and molecular dynamics simulation were carried out using Forcite module in Materials Studio 8.0 [40] from Accelrys Inc. The Fe (1 1 0) surface with a slab of 10 Å and a simulation box of dimensions 27.31 × 27.31 × 66.13 Å was constructed with the help of Visualizer, Amorphous cell and discover modules implemented in BIOVIA Materials Studio package. The interaction of mercaptoalcohol molecules with the metal surface was
investigated in the three-dimensional box. Molecular dynamics simulation were performed at temperatures $T = 298$ K maintained constant by the Andersen thermostat and a time step of 0.5 fs and the ensemble with atom number, system volume, temperature fixed (NVT) and a simulation time of 2000 ps to reach simulation system under an equilibrium state. The Condensed-phase Optimized Molecular Potential for Atomistic Simulation Studies (COMPASS II) force field was chosen for the energies minimization and molecular dynamics simulation [41]. The extent of the interactions of the corrosion inhibitor molecules adsorbed onto the Fe(1 1 0) surface can be demonstrated by their interaction energy estimated using the following equation:

$$E_{\text{ads}} = E_{\text{tot}} - (E_{\text{sur}} + E_{\text{inh}}), \quad (9)$$

where $E_{\text{tot}}$ is the total energy of the surface and inhibitors, $E_{\text{sur}}$ and $E_{\text{inh}}$ are the surface energy and the energy of inhibitor molecule, respectively.

**RESULT AND DISCUSSION**

*Molecular Geometry*

The optimized structures with M06-2x method and the 6-311++G** basis set were presented in Fig. 1. The corresponding bond lengths, bond angles, and torsional angles of mercaptoalcohol molecules were listed in Table 1. It can be observed that with the increasing of the length of carbon chain, there is little difference of these mercaptoalcohol molecules in the bond lengths and the bond angles. The bond lengths of H–S and H–O in these ten molecules are about 1.34 and 0.96 Å, respectively. The bond lengths of S–C and O–C bonds are around 1.83 and 1.42 Å, respectively. And the bond angles of H–S–C and H–O–C are changing within the range of 96.40°–97.3° and 109.05°–109.3°. The direction of the –SH and –OH in C_3 molecule is slightly different from that in other molecules. The direction of the H atoms connecting to S and O atoms in C_7 and C_9 molecule slightly differ from that in other molecules. The torsional angles of H–S–C_n–C_{n−1} and H–O–C1–C2 are 23.6° and 0.8° for C_2; while the corresponding torsional angles for other molecules are near zero. To decrease the repulsion potential energy, the S atom and the O atom have to take a different orientation keeping a larger distance. As a result, the intramolecular interaction between S atom and O atom in mercaptoethanol is too strong to be neglected; while the interaction in the other molecules is weak enough to be neglected. So the S–C bond is not in the same plane with the O–C bond in C_2.

### Molecular Reactivity

According to the frontier orbital theory, HOMO indicates the distribution of highest energy electrons in the molecule, and these electrons will transfer to electron-deficient materials such as metal surfaces, while LUMO indicates that the molecule has the ability to accept electron [42, 43]. The distribution of HOMO and LUMO obtained at the M06-2x/6-311++G** level were presented in Fig. 1.

As is shown in Fig. 1, HOMO is mainly localized on –SH group, indicating that the linear mercaptoalcohol molecules mainly supplies electrons from the –SH end to the empty orbital of the metal atom. The LUMO is distributed almost throughout the molecule. As the carbon chain grows, LUMO gradually delocalizes to the hydrophilic groups at both ends, indicating that both ends can accept lone electrons from the metal surface [44]. The –SH group can simultaneously supply electrons to the metal surface and accept electrons from metal atoms, indicating that –SH is easier adsorbed on the metal surface than –OH group. The oxygen atom can also be adsorbed onto the metal surface because of its lone electron pairs in –OH group.

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**Table 1. Structural parameters of mercaptoalcohol molecules calculated at the M06-2x/6-311++G** level**

| Inhibitor | C_2  | C_3  | C_4  | C_5  | C_6  | C_7  | C_8  | C_9  | C_10 | C_11 |
|-----------|------|------|------|------|------|------|------|------|------|------|
| Bond, Å   |      |      |      |      |      |      |      |      |      |      |
| H–S       | 1.340| 1.342| 1.341| 1.342| 1.342| 1.341| 1.342| 1.342| 1.342| 1.341|
| S–C       | 1.828| 1.829| 1.831| 1.830| 1.830| 1.830| 1.830| 1.830| 1.830| 1.830|
| O–C       | 1.417| 1.417| 1.419| 1.418| 1.419| 1.419| 1.419| 1.419| 1.419| 1.419|
| H–O       | 0.960| 0.959| 0.959| 0.959| 0.959| 0.959| 0.959| 0.959| 0.959| 0.959|

| Angle, deg |      |      |      |      |      |      |      |      |      |      |
| H–S–C     | 96.5 | 96.5 | 96.9 | 96.9 | 96.9 | 96.9 | 97.2 | 97.1 | 97.0 | 97.0 |
| H–O–C     | 109.2| 109.2| 109.2| 109.3| 109.2| 109.1| 109.0| 109.1| 109.1| 109.2|

| Torsional angle, deg |      |      |      |      |      |      |      |      |      |      |
| H–S–C_n–C_{n−1}     | 23.6 | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  |
| H–O–C1–C2           | 0.8  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  |
All quantum-chemical parameters of the mercaptoalcohol molecules were listed in Table 2. The $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ are useful to elucidate the chemical reactivity of a molecule. According to the frontier molecular orbital theory, the chemical reactivity of a molecule is related to the transition of electrons from the HOMO to the LUMO [45]. The higher the energy level of HOMO is, the stronger the interaction between the inhibitor and the metal material is. The stronger interaction shows the inhibitor is more likely to be adsorbed onto the metal surface, hence a better corrosion inhibition performance [46]. Similarly, the energy level of the LUMO indicates the ability to accept electrons of a molecule [47]. As is shown in Table 2, the energy level of HOMO of molecules with even carbon chain $C_2, C_4, C_6, C_8, C_{10}$ is gradually increasing, while the energy level of LUMO of those molecules is gradually decreasing. The same is true for molecules with odd carbon chain $C_3, C_5, C_7, C_9, C_{11}$: the energy level of HOMO increases while that of LUMO decreases. $C_{11}$ molecule has the highest HOMO energy level and the lowest LUMO energy level. As a result, the interaction between $C_{11}$ molecule and the metal material is the strongest.

The energy gap $\Delta E$ is an important parameter to illustrate the reactivity tendency of molecules to interact with the metal. The lower the $\Delta E$ is, the higher the reactivity of molecules is [48]. Thus, $\Delta E$ has been used as an important index to measure the binding ability of molecules with the metal surface. It can be seen from Table 2 that the binding ability of the molecules with even carbon chain $C_2, C_4, C_6, C_8, C_{10}$ gradually increases; the binding ability of the molecules with odd carbon chain $C_3, C_5, C_7, C_9, C_{11}$ also increases gradually. $C_{11}$ has the lowest energy gap, so it has the highest reactivity.

Fig. 1. (Color online) The optimized structures and the distribution of HOMO and LUMO in mercaptoalcohol molecules calculated at the M06-2x/6-31++G** level.
The dipole moment (μ) of a molecule is also an important parameter to elucidate the chemical reactivity of a molecule. Literature [49, 50] survey reveals that as values of the dipole moment increase, the adsorption process is further facilitated. As is shown in Table 2, for molecules with even carbon chain C_2, C_4, C_6, C_8, C_10, the dipole moment is gradually increasing; while for molecules with odd carbon chain, the dipole moment reaches a minima when the carbon chain lengthens to seven. That may be result from the change of the molecular symmetry and the orientation of the hydrogen atoms connecting to S and O atoms. The electronegativity of oxygen is higher than that of sulfur. One can see that the orientation of the hydrogen atoms connecting to S and O atoms in C_7 and C_9 is different from that of the other molecules. From the perspective of the dipole moment, the values of dipole moment of molecules C_3, C_5, C_7 and C_9 is different from that of the other molecules. From the perspective of the dipole moment, the values of dipole moment of molecules C_3, C_5, C_7 and C_9 is different from that of the other molecules. From the perspective of the dipole moment, the values of dipole moment of molecules C_3, C_5, C_7 and C_9 is different from that of the other molecules. From the perspective of the dipole moment, the values of dipole moment of molecules C_3, C_5, C_7 and C_9 is different from that of the other molecules. From the perspective of the dipole moment, the values of dipole moment of molecules C_3, C_5, C_7 and C_9 is different from that of the other molecules. From the perspective of the dipole moment, the values of dipole moment of molecules C_3, C_5, C_7 and C_9 is different from that of the other molecules. From the perspective of the dipole moment, the values of dipole moment of molecules C_3, C_5, C_7 and C_9 is different from that of the other molecules. From the perspective of the dipole moment, the values of dipole moment of molecules C_3, C_5, C_7 and C_9 is different from that of the other molecules.

The three parameters including electrophilicity (χ) [35, 51], global hardness (η), and global softness (σ) present the ability of molecules to accept/donate electrons. Global softness (σ) is a predominant parameter to characterize the ability of molecules to be adsorbed. The higher the value, the more likely it is to be adsorbed. The case for electrophilicity (χ) and global hardness (η) is in contrast to that of global softness (σ): the lower the values are, the more likely it is to be adsorbed. From Table 2, it could be concluded that C_11 is the molecule that is the most likely to be adsorbed. These results are in accordance with the conclusion obtained from the frontier molecular orbital.

The Mulliken charge distribution of mercaptoalcohol molecules was calculated at the M06-2x/6-311++G** level, and its local active sites were discussed by Fukui function. The Mulliken charge distribution of some heavy atoms is shown in Table 3. The charge of S atom in the molecules first increases gradually and reaches the peak in C_7, and then begins to decrease gradually. The intramolecular interaction of C_7 is weaker than that of other molecules and the negative charge located on S atom becomes more dispersed. So the change in C_7 is the largest. Due to the negative charge in both S and O atoms, all molecules can be adsorbed. As is shown in Table 3, the nucleophilic index of S is large, which indicates that the molecules have nucleophilic activity. The results of the quantum chemical calculation indicate that the molecule C_11 is the most easily adsorbed.

### Theoretical Corrosion Inhibition Efficiency

Based on the inhibition efficiency of C_2 obtained experimentally and the calculated quantum chemical parameters, we determined the theoretical inhibition efficiency of the molecules using the following formula:

\[
I_{\text{add}}\% = \frac{I_{c_2} - I_{c_x}}{I_{c_2}} \times 100\%, \quad (10)
\]

\[
E\% = \frac{E_{c_x} - E_{c_2}}{E_{c_2}} \times 100\%, \quad (11)
\]

\[
IE_{\text{add}}\% = E_{\text{add}}\% \times IE_{c_2}\%, \quad (12)
\]

\[
IE_{\text{theor}}\% = I_{\text{add}}\% + IE_{\text{add}}\% + IE_{c_2}\%, \quad (13)
\]
where $I_{\text{add}}\%$ is the percentage ionization potential of the additive for model (C_2), $E\%$ is the percentage energy of the additive for model (C_2), $IE_{\text{add}}\%$ is the inhibition efficiency of the additive, and $IE_{\text{theor}}\%$ is the theoretical inhibition efficiency.

The theoretical corrosion inhibition efficiency of the mercaptoalcohol molecules was presented in Table 4. As is shown in Table 4, the theoretical inhibition efficiency is in agreement with the experimental results of molecules C_2, C_3, C_6, C_9, which proves that the calculation formula are reasonable. But what needs to be noticed is that the theoretical inhibition efficiency for C_3 is bigger than that of C_2, but the experimental result is smaller. That maybe resulted from the different environment and the different direction of –SH and –OH in the two molecules. The molecules are exposed to CO_2 saturated aqueous solution with sodium chloride in experiment. Single molecule in the gas phase were considered in this work because the aim of this work is to analyze the structure–activity relationship of mercaptoalcohol. The theoretical inhibition efficiency increases with the increasing of carbon chain length. In the following work, we are simulating the corrosion inhibition performance in aqueous solution. That is to say, the C_11 molecule as corrosion inhibitor has the best corrosion inhibition performance.

### Molecular Dynamics Simulation

Currently, a large number of literature on corrosion inhibitor include the use of molecular dynamics simulation as a modern tool for studying the interaction between inhibitors and metal surfaces [39, 53]. In this study, molecular dynamics simulation studies were designed to predict the binding strength of linear mercaptoalcohol compounds on iron surfaces and to determine if there is a clear correlation between the binding energy of these inhibitors and experimental determination. The equilibrium adsorption configurations of all mercaptoalcohol molecules on Fe (1 1 0) surface were presented in Fig. 2.

As is shown in Fig. 2, both –SH and –OH groups are adsorbed onto the surface Fe (1 1 0) because O and S atoms have lone electrons pairs. When the system reach its adsorption equilibrium, the molecular plane is parallel to the Fe (1 1 0) surface. Furthermore, one can see that the orientation of the S–C and O–C bonds in molecule C_2 is different from the orientation of the two bonds in other molecules. In C_2, the distance between the S atom and the O atom is too short to ignore the repulsion interaction. According to the variation principle, the energy of a system is lower, the system is more stable. To decrease the energy of the molecule, the S atom and the O atom have to take a different orientation keeping a larger distance to

### Table 3. Fukui indices of the mercaptoalcohol molecules calculated at the M06-2x /6-311++G** level using Mulliken population analysis

| Molecule | Atom | Charge | $f^+_{\text{add}}$ | $f^-_{\text{add}}$ | Molecule | Atom | Charge | $f^+_{\text{add}}$ | $f^-_{\text{add}}$ |
|----------|------|--------|-----------------|-----------------|----------|------|--------|-----------------|-----------------|
| C_2      | C_1  | -0.022 | -0.046          | -0.025          | C_7      | C_1  | -0.382 | -0.255          | -0.201          |
|          | C_2  | -0.220 | -0.443          | -0.265          | C_7      | C_7  | -0.420 | -0.418          | -0.245          |
|          | O    | -0.229 | -0.104          | -0.054          | O        | O    | -0.250 | -0.250          | -0.402          |
|          | S    | -0.070 | 0.491           | -0.396          | S        | S    | -0.192 | 0.362           | -0.283          |
| C_3      | C_1  | -0.243 | -0.441          | -0.228          | C_8      | C_1  | -0.072 | -0.208          | -0.192          |
|          | C_3  | -0.347 | -0.001          | 0.366           | C_8      | C_8  | 0.104  | -0.208          | -0.197          |
|          | O    | -0.289 | -0.279          | -0.392          | O        | O    | -0.273 | -0.265          | -0.403          |
|          | S    | -0.117 | 0.461           | -0.362          | S        | S    | -0.207 | 0.369           | -0.096          |
| C_4      | C_1  | -0.311 | -0.424          | -0.234          | C_9      | C_1  | -0.360 | 0.005           | 0.071           |
|          | C_4  | -0.401 | -0.006          | 0.084           | C_9      | C_9  | -0.427 | -0.424          | -0.274          |
|          | O    | -0.281 | -0.278          | -0.397          | O        | O    | -0.241 | -0.259          | -0.398          |
|          | S    | -0.146 | 0.420           | -0.270          | S        | S    | -0.120 | 0.343           | -0.128          |
| C_5      | C_1  | -0.315 | -0.242          | -0.223          | C_10     | C_1  | -0.428 | -0.242          | -0.217          |
|          | C_3  | -0.382 | -0.012          | -0.099          | C_10     | C_10 | -0.208 | -0.208          | -0.192          |
|          | O    | -0.274 | -0.268          | -0.396          | O        | O    | -0.263 | -0.274          | -0.400          |
|          | S    | -0.159 | 0.410           | -0.318          | S        | S    | -0.129 | 0.360           | -0.241          |
| C_6      | C_1  | -0.175 | -0.209          | -0.177          | C_11     | C_1  | -0.591 | -0.417          | -0.258          |
|          | C_6  | -0.321 | -0.245          | -0.169          | C_11     | C_11 | -0.491 | -0.020          | 0.103           |
|          | O    | -0.272 | -0.266          | -0.398          | O        | O    | -0.268 | -0.262          | 0.045           |
|          | S    | -0.176 | 0.392           | -0.288          | S        | S    | -0.236 | 0.358           | -0.267          |
decrease the repulsion potential energy. When the length of the carbon chain reaches to three carbons, the repulsion potential is weak enough to be ignored. So the S–C bond is in the same plane with the O–C bond keeping the system stable in all molecules besides C_2. To analyze the adsorption performance, the adsorption energies were calculated and listed in Table 5. As is shown in Table 5, the absolute values of the adsorption energies increase with the lengthening of carbon chain. The longer the carbon chain is, the easier the molecule is to be adsorbed onto the Fe (1 1 0) surface. C_11 has the longest carbon chain, the interaction between C_11 and the Fe (1 1 0) surface is the strongest. The molecular dynamics simulation result is in agreement with that of the quantum chemical calculation.

To further analyze the interaction between the molecules and the Fe (1 1 0) surface, the distance between the S atom and the Fe(1 1 0) surface and the distance between the O atom and the Fe (1 1 0) surface were presented in Table 6. As is shown in Table 6, all distances are about 3 Å, which shows that the interaction between the molecule and the Fe (1 1 0) surface is weaker than that of a chemical bond. M. Volmer-Uebing [11] proposed that the chemisorptive bonds between the substrate and the thiol could be formed probably by only cleaving the S–H bond in nitrogen purged aqueous. But the molecular dynamics simulation was performed in vacuum in the present study, and the S–H bond is difficult to cleave. At the same time, the proton with a weak steric hindrance effect for its small volume partly separates the sulfur atom and O atom from the Fe (1 1 0) surface in Fig. 2. So the interaction between the mercaptoalcohol molecule and the Fe (1 1 0) surface is weaker than that of a chemical bond. Furthermore, the distance becomes shorter and shorter with the lengthening of the carbon chain. The distance of the C_11 molecule and the Fe (1 1 0) surface is the shortest. As a result, the interaction between C_11 and the Fe (1 1 0) surface is the strongest. The molecular dynamics simulation result is in agreement with that of the quantum chemical calculation.

The experimental corrosion inhibition efficiency determined in [52].

| Molecule | I, % | E, kcal mol\(^{-1}\) | IE_add, % | IE_theor, % | IE_exp, % |
|----------|------|-----------------|----------|-------------|----------|
| C_2      | 0.223| 8.076           | —        | —           | 54.30    |
| C_3      | 0.211| 8.023           | —        | 7.09        | 58.81    |
| C_4      | 0.252| 7.979           | 1.2011   | 14.19       | 63.21    |
| C_5      | 0.220| 7.983           | 1.1516   | 21.29       | 67.01    |
| C_6      | 0.252| 7.970           | 1.3125   | 28.39       | 71.03    |
| C_7      | 0.249| 7.958           | 1.4611   | 35.49       | 75.03    |
| C_8      | 0.277| 7.944           | 1.6345   | 42.59       | 79.06    |
| C_9      | 0.271| 7.937           | 1.7211   | 49.69       | 83.00    |
| C_10     | 0.287| 7.931           | 1.7954   | 56.79       | 86.93    |
| C_11     | 0.293| 7.928           | 1.8326   | 63.89       | 90.83    |

| Molecule | E_{tot}, kcal mol\(^{-1}\) | E_{ads}, kcal mol\(^{-1}\) | Molecule | E_{tot}, kcal mol\(^{-1}\) | E_{ads}, kcal mol\(^{-1}\) |
|----------|-----------------|-----------------|----------|-----------------|-----------------|
| C_2      | −31590.80       | −43.17          | C_7      | −31713.43       | −89.86          |
| C_3      | −31620.60       | −51.46          | C_8      | −31738.50       | −97.99          |
| C_4      | −31686.48       | −63.80          | C_9      | −31692.30       | −111.54         |
| C_5      | −31693.25       | −73.10          | C_10     | −31751.57       | −122.44         |
| C_6      | −31622.00       | −78.65          | C_11     | −31766.98       | −130.47         |

CONCLUSIONS

The structure–activity relationship of mercaptoalcohol molecules as corrosion inhibitors for carbon steel was investigated using quantum chemistry calculation and molecular dynamics simulation (MD). The geometry optimization and calculation of the quantum chemistry parameters such as the energy of the highest occupied molecular orbital and the energy of the lowest unoccupied molecular orbital, electronegativity (χ), dipole moment (μ) were performed at the M06-2x/6-311++G** level. Quantum chemical calculation results indicate that the corrosion inhibition
The performance of the mercaptoalcohol molecules is enhanced with the lengthening of the carbon chain. And the C_11 molecule shows a best theoretical inhibition efficiency. At the same time, molecular dynamics simulation results indicate that the mercaptoalcohol molecular plane is parallel to the Fe (1 1 0) surface and both the –SH and the –OH are able to be adsorbed onto the Fe (1 1 0) surface.

The values of the adsorption energy show that the longer of the carbon chain is, the molecule is easier to be adsorbed onto the Fe (1 1 0) surface. The trend of the changing of the theoretical corrosion inhibition efficiency is in agreement with that of the experimental result. The predicted theoretical corrosion inhibition performance of C11 molecule as corrosion inhibitor is the best.
Table 6. The distance (Å) between O and S atoms in the mercaptoalcohol molecules and the Fe (1 1 0) surface

| Molecule | O-Fe (1 1 0) | S-Fe (1 1 0) | Molecule | O-Fe (1 1 0) | S-Fe (1 1 0) |
|----------|-------------|-------------|----------|-------------|-------------|
| C_2      | 3.116       | 3.545       | C_7      | 3.078       | 3.248       |
| C_3      | 3.174       | 3.427       | C_8      | 3.047       | 3.125       |
| C_4      | 3.139       | 3.371       | C_9      | 3.036       | 3.115       |
| C_5      | 3.128       | 3.362       | C_10     | 2.992       | 3.111       |
| C_6      | 3.126       | 3.327       | C_11     | 2.930       | 2.974       |

ACKNOWLEDGMENTS

Project Grants to Scientific Research Innovation Team of Universities Affiliated to Sichuan Province (no. 18TD0012) and Applied Basic Research Program of Science and Technology Department of Sichuan Province (grant no. 2017JY0044).

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