



## Theoretical Understanding of Quaternary Ammonium Surfactant Corrosion Inhibitor in Acetic Acid Media: Computer Modelling

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### ABSTRACT

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Corrosion inhibitor (CI) is one of the corrosion control strategies commonly used in controlling the corrosion rate of metal equipment used in oil and gas production facilities. An in-depth analysis of the inhibition mechanism of CI molecules on the metal surface is crucial in understanding the corrosion theory. Hence, this study uses density functional theory (DFT) calculation and molecular dynamic (MD) simulation to investigate the inhibition mechanism of two quaternary ammonium cationic surfactant CI molecules, C6 and C8. Both CI molecules show a high reactivity in DFT calculation with a low band gap energy value (1.26 eV). The cationic ammonium of both CI molecules is the reactive region that donates electrons to the empty 3d orbital at a metal surface. Results from the MD simulation show that C8 CI molecules have a better inhibition property with a higher adsorption energy value. Other parameters, such as diffusion coefficient and molecular aggregation, are also used in explaining both CI properties as a corrosion inhibitor. The theoretical understanding analysis of the inhibition properties of CI molecules using computational methods can be used as a screening process for the future development of CI molecules that are more cost and time-friendly.

## 1. Introduction

Oil and gas and production companies have encountered corrosion problems in the equipment of storage, transportation and many more facilities. The complex procedures in oil and gas production yield various substances that enhance corrosion, such as dissolved hydrogen sulphide (H<sub>2</sub>S), carbon dioxide (CO<sub>2</sub>), and oxygen (O<sub>2</sub>) gaseous [1]. The report by NACE in 2013 stated that the global cost of corrosion is estimated to be US\$2.5 trillion, equivalent to 3.4% of the global Gross Domestic Product (GDP). The same report also stated that 15 to 35% of the cost of corrosion could be saved by using the available corrosion control particles. Corrosion inhibitor (CI) is a common corrosion control particle used as an economical and effective way of mitigating internal corrosion [2-4]. CI are broadly classified as anodic, cathodic, or mixed corrosion inhibitors and can be classified

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on their chemical natures, such as organic or inorganic ones [5]. The organic type of CI molecules, such as surfactants, are widely used in industry because of their effectiveness in a wide range of temperatures, good oil/water solubility, compatibility with protected materials, low costs, and relatively low toxicity [6].

A recent finding by Zheng *et al.*, (2022) has proven the ability of cationic ammonium surfactants CI dodecyl trimethyl ammonium bromide (DTAB), dodecyl dimethyl benzyl ammonium bromide (DDBAB) that able to inhibit corrosion up to 94.98 % on Q235 steel in sulfuric acid media [7]. In 2019, Gao *et al.*, also found that the quaternary ammonium cationic surfactants, dodecyl trimethyl ammonium chloride (DTAC), capable of mitigating corrosion with inhibition efficiency that can exceed 90 % in the presence of hydrochloric acid compared to CI with a longer alkyl chain length. DTAC surfactant CI molecules with a shorter chain length ease the adsorption of the molecule on the metal surface and increase the inhibition efficiency. The findings have found that percentage inhibition efficiency is affected by the properties and strength of the adsorption of the CI molecules [8]. An in-depth study on the adsorption of surfactant CI molecules will better explain the inhibition mechanism of the CI molecules on the metal surface. A review by Numin *et al.*, (2022) has stated the importance of an in-depth investigation of the surfactant CI molecules as a corrosion inhibitor and, at the same time, the lack of study in the presence of organic acid media, which a substance that can enhance corrosion in the oil and gas production process [9]. Thus, this study focused on the in-depth study of the adsorption mechanism of the quaternary ammonium surfactants (C6 and C8) towards the metal surface, Fe (110) in the presence of hydrochloric acid (HCl) and acetic acid via DFT calculation and MD simulation.

## 2. Methodology

### 2.1 Density Functional Theory (DFT) Calculation

DFT calculation is a quantum-mechanical method used in chemistry and physics to calculate the electronic properties of atoms, molecules, and solids (Putrajaya 5). The DFT calculation technique determined the reactivity and adsorption properties of the CI molecules. The structure of quaternary ammonium cation surfactant molecules, C6 and C8, are shown in Table 1. The TURBUMOLE (Tmolex) software was used to run the DFT calculation. The molecules are optimized using a hybrid functional B3LYP [10,11] in a non-aqueous or vacuum environment with a def-SV(P).h basis set [12,13]. The ground-state calculation was inserted under the DFT setting to generate the input file. The molecule's visualization and parameters derived from the DFT calculation were visualized and calculated by the Tmolex program.

The frontier molecular orbitals, highest occupied molecular orbital energy ( $E_{HOMO}$ ) and the lowest unoccupied molecular orbital energy ( $E_{LUMO}$ ) used to explain electron transfer and the reactive region of the CI molecules.  $E_{HOMO}$  and  $E_{LUMO}$  that calculated from the DFT calculation can be derived to another parameters to explain the CI molecule's adsorption properties. The parameters are band-gap energy ( $\Delta E$ ), number of transferred electron ( $\Delta N$ ), electronegativity ( $\chi$ ), hardness ( $\eta$ ), softness ( $\sigma$ ), ionization potential ( $I$ ) and electron affinity ( $A$ ).

The frontier molecular orbitals, highest occupied molecular orbital energy ( $E_{HOMO}$ ) and the lowest unoccupied molecular orbital energy ( $E_{LUMO}$ ) are used to explain electron transfer and the reactive region of the CI molecules. HOMO and LUMO energy calculated from the DFT calculation can be derived into other parameters to explain the CI molecule's adsorption properties. The parameters are band-gap energy ( $\Delta E$ ), number of transferred electrons ( $\Delta N$ ), electronegativity ( $\chi$ ), hardness ( $\eta$ ), softness ( $\sigma$ ), ionization potential ( $I$ ) and electron affinity ( $A$ ). The band gap energy, ionization potential, and electron affinity can be calculated according to the Eq. (1)-(3), respectively [14]

$$\Delta E = E_{LUMO} - E_{HOMO} \quad (1)$$

$$I = -E_{HOMO} \quad (2)$$

$$A = -E_{LUMO} \quad (3)$$

Then, the calculated ionization potential and electron affinity are used to calculate the electronegativity and chemical hardness using the following Eq. (4) and Eq. (5) [15]

$$\chi = \frac{I+A}{2} \quad (4)$$

$$\eta = \frac{I-A}{2} \quad (5)$$

Other than that, the other parameter is the global chemical softness ( $\sigma$ ) where it can describe the capacity if an atom or groups of atoms to receive electrons, was calculated by using the following equation [16]:

$$\sigma = \frac{1}{\eta} = \frac{2}{E_{HOMO}-E_{LUMO}} \quad (6)$$

The number of transferred electrons from ammonium surfactant cationic Cl molecules to the metal surface was also calculated by using the  $\chi$  and  $\eta$  value of the Cl molecules and the composition of the metal (Eq. (7)). The  $\chi_{inh}$ ,  $\chi_{Fe}$ ,  $\eta_{inh}$ , and  $\eta_{Fe}$  indicate the electronegativity of Cl, the electronegativity of iron (Fe) metal, the chemical hardness of Cl, and the chemical hardness of Fe metal, respectively. The theoretical value of  $\chi_{Fe}$  is 7.0 eV, and  $\eta_{Fe}$  is 0 eV [17,18].

$$\Delta N = \frac{\chi_{Fe}-\chi_{inh}}{2(\eta_{Fe}+\eta_{inh})} \quad (7)$$

## 2.2 Molecular Dynamic (MD) Simulation

MD simulation is typically conducted to obtain the equilibrium properties of the system. In the corrosion system, the Cl molecule will be surrounded by the corrosion solution and positioned next to the metal surface to reach the most stable state of the Cl molecule. As a result, MD simulation can provide the strength of adsorption, diffusion coefficient, and aggregation of Cl molecules in different concentrations [19]. GROMACS software package 4.5 were used throughout this study with the GROMOS molecular force fields. The optimized geometry and topology file of all molecules in the simulation systems are obtained from the Automated Topology Builder (ATB) and Repository Version 3.0 server [20]. In the calculation of adsorption energy, 1 Cl molecule was packed together in the simulation box. In contrast, the molecules were added in different concentrations (0.04 M, 0.08 M, 0.12 M, 0.16 M, and 0.20M) for the diffusion coefficient and molecular aggregation analysis. The box size used in this simulation is (51.60, 51.60, 77.40) Å, and the corrosion systems include Fe (110) as a metal surface, 1 M HCl, and 500 ppm acetic acid as an acid condition solution.

The energy minimization was performed to begin the simulation using the steepest descent followed by conjugate gradient methods for 5000 steps. The simulation then proceeded with the 5 ns of NVT to establish the proper orientation in the system's temperature for the adsorption's energy calculation. Then, the NPT ensemble was run for 5 ns to analyse the molecular aggregation of Cl

molecules in the corrosion particles. Throughout this study, all the simulations were computed using GROMACS software package 4.5 with the GROMOS molecular force fields. Periodic boundary condition (PBC) was applied in all directions (x, y, z) with 2.0 fs time steps. Electrostatic interaction was calculated using Particle Mesh Ewald (PME) [21] with a grid spacing of 0.12 nm and fourth-order interpolation. The Coulomb and Lennard interactions were summed up to 1.2 nm. The neighbour searching of 1.2 nm was updated every five steps. The bond lengths for solute as well as organic solvent molecules were constrained with Linear Constraint Solver (LINCS) [22], while for all water molecules, is SETTLE algorithm [23].

### 3. Results

#### 3.1 Density Functional Theory (DFT) Calculation

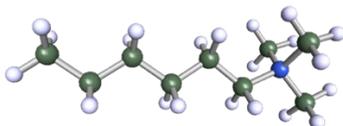
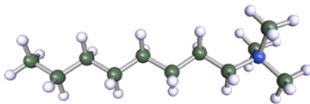
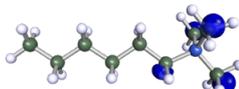
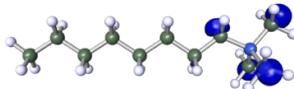
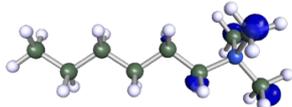
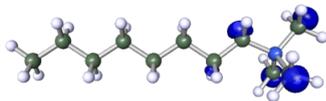
The adsorption properties of the CI molecules towards the metal surface are studied by DFT calculation. The reactive region of the CI molecules to donate and receive electrons are explained by their HOMO and LUMO behaviour, respectively. The optimized structure, HOMO and LUMO of the two ammonium cationic surfactant CI molecules are shown in Table 1. It is shown that the HOMO and LUMO region are distributed at the alpha carbon of the quaternary ammonium group, representing the ability of these parts of the molecule to donate and receive electrons towards and from the metal surface. The properties of quaternary cationic ammonium with a lone pair of electrons give the donation ability of that region to the empty d orbital of metal, and the alpha carbon can act as an electrophile to accept electrons from the metal surface through a back-donation mechanism [24]. The HOMO and LUMO energy calculated by DFT calculation and the other parameters derived from these energy values are tabulated in Table 2. The table shows that both C6 and C8 CI molecules have a lower band gap energy value denotes the high reactivity of these molecules to undergo an electron transfer mechanism with the metal surface. Between all parameters in Table 2, band gap energy is one of the essential values that can correlate with the inhibition efficiency of the CI molecules. Several studies have proved that CI molecules with a lower band gap energy can work as better corrosion inhibitors [25] [9]. A study by Han *et al.*, in 2020 has confirmed that Gemini surfactants named DBP, which has the lowest band gap energy value (2.472 eV) compared to the other CI molecules, gave the highest inhibition efficiency value (91.76%) [25]. A same value of the band gap energy value between C6 and C8 in Table 2 indicates the minor effect on their reactivity with a different alkyl chain length. It implies that the reactivity of both quaternary cationic ammonium surfactant CI molecules is only affected by the hydrophilic part of the molecules.

The tendency to donate and accept electrons of C6 and C8 CI molecules is explained using the HOMO and LUMO energy values, respectively. The HOMO and LUMO energy of C8 is slightly higher than the C6 molecule, indicating a higher tendency to donate and accept electrons, respectively, for the C8 molecule. The electronegativity values for both CI molecules also show that C8 has a higher tendency to donate electrons with a lower value than the C6 CI molecule. Electronegativity is defined as the tendency of a molecule to attract electrons toward itself [26]; the lower value of C8 indicates the higher tendency for this molecule to donate electrons. The same hardness and softness value for both CI molecules represent the resistance towards the deformation of electron cloud around the molecules [16] and the capacity of an atom or groups of atoms to receive electrons [15], respectively, are not affected by the different of alkyl chain length of the quaternary cationic ammonium surfactant CI molecules. The number of transferred electrons is the final output parameter derived from the HOMO and LUMO energy calculated by DFT calculation. The positive value indicates the significant electron transfer process from CI molecules to the iron metal surfaces [27]. So, the DFT calculation has found that the C8 surfactant CI molecule that has a higher alkyl chain length compared

to C6 has a better electron donating ability towards the metal surface and assume to have a better inhibition efficiency. A study by Negm *et al.*, also stated that the addition of a longer alkyl chain length of the quaternary ammonium surfactant CI could work better as a CI with a higher inhibition efficiency [28].

**Table 1**

The optimized structure, HOMO and LUMO of all quaternary ammonium cationic surfactant CI molecules

Structures	Corrosion Inhibitor Molecules	
	C6	C8
Optimized molecule		
HOMO		
LUMO		

**Table 2**

Calculated DFT calculation of all quaternary ammonium cationic surfactant CI molecules

Structures	Corrosion Inhibitor Molecules	
	C6	C8
$E_{HOMO}$ , eV	-0.2966	-0.2939
$E_{LUMO}$ , eV	0.9660	0.9687
$\Delta E$ , eV	1.2626	1.2626
Ionization Potential, $I$	0.2966	0.2939
Electron Affinity, $A$	-0.9666	-0.9687
Global Hardness, $\eta$	0.6313	0.6313
Electronegativity, $\chi$	-0.3347	-0.3374
Softness, $\sigma$	1.5840	1.5840
Fraction of Transferred Electron, $\Delta N$	5.8092	5.811

### 3.2 Molecular Dynamic (MD) Simulation

MD simulation method was used to investigate the adsorption strength, diffusion coefficient, and molecular aggregation of C6 and C8 CI molecules at acidic conditions, 1 M HCl, 500 ppm acetic acid solutions, and the Fe (110) were used to represent the metal surface.

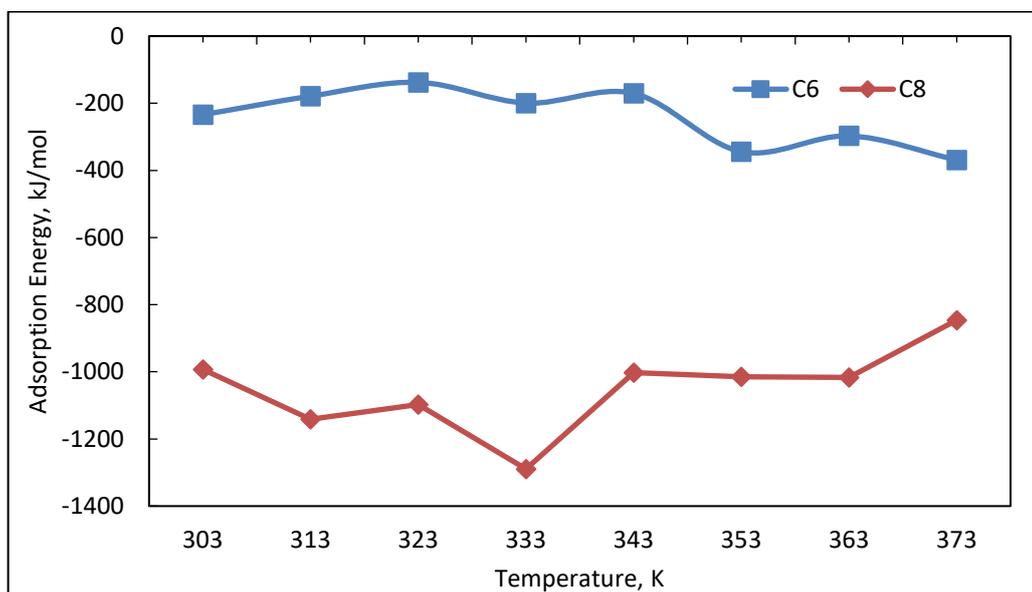
#### 3.2.1 Adsorption energy

In adsorption energy ( $E_{ads}$ ) calculation, three different systems were constructed; 1. system with only CI molecule ( $E_{inhibitor}$ ), 2. corrosion system without CI molecule ( $E_{surface+solution}$ ), and 3. corrosion system with CI molecule ( $E_{total}$ ). The adsorption energy was calculated in different temperatures from 303 to 373 K. The equation used to calculate the adsorption energy ( $E_{ads}$ ) are as follow (8) [29]:

$$E_{ads} = E_{total} - (E_{surface+solution} + E_{inhibitor}) \quad (8)$$

where the  $E_{total}$  is the energy for corrosion system with CI molecule,  $E_{surface+solution}$  is the energy for corrosion system without CI molecule, and  $E_{inhibitor}$  is the energy of the system with CI molecule only. The calculated adsorption energy of C6 and C8 molecules is displayed in Figure 1. The adsorption strength of the CI molecules is based on the more negative value of adsorption energy, where the higher the adsorption energy negative value, the higher the strength of adsorption of the CI molecules towards the Fe (110) metal surface [30].

Figure 1 shows that C8 CI molecules have a higher negative value of adsorption energy at all temperature conditions than C6 molecules, indicating the higher strength of adsorption of the C8 molecule towards the Fe (110) metal surface. Based on the HOMO and LUMO region from DFT calculation, the adsorption mechanism of the CI molecules mainly happens at the positively charged nitrogen with a lone pair of electrons and the alpha carbon next to the nitrogen atom. The reactive region of the CI molecules is also known as the hydrophilic region that can form an interaction through the electron donation to the Fe (110) metal empty 3d orbitals [31]. On the other hand, the alkyl chain or the hydrophobic part of the surfactant CI molecules will extend away from the metal surface to the corrosion particles solution and form an array of hydrophobic tails that replace the corrosion particles and provide further protection on the metal surface [32,33]. That is why the adsorption strength of the C8 molecule is higher than C6 due to the longer alkyl chain length for molecule C8 than C6. Results from adsorption energy calculation also correlate with the results from DFT calculation, where the C8 molecules with a longer alkyl chain length have a higher tendency to donate electrons than the C6 molecule.



**Fig. 1.** The adsorption energy of C6 and C8 corrosion inhibitors with temperatures between 303 to 373 K towards Fe (110) metal surface calculated via MD simulation

### 3.2.2 Molecular aggregation

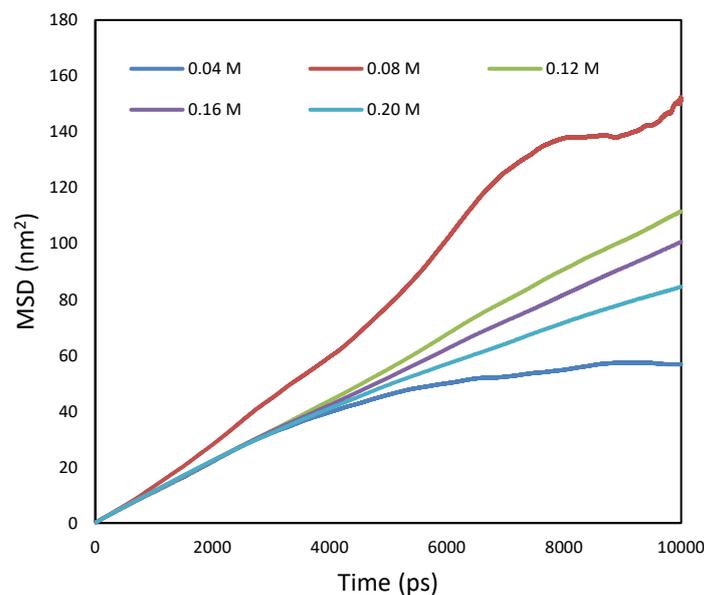
The diffusion coefficient is calculated in the molecular aggregation analysis, and the behaviour of the CI molecules in the corrosion particles is observed. Five different systems with different concentrations (0.04 M, 0.08 M, 0.12 M, 0.16 M, and 0.20 M) of CI molecules in acidic conditions containing 1 M HCl, and 500 ppm acetic acid solutions, at temperature 333 K. In the diffusion

coefficient calculation, the mean square displacement (MSD) as a function of time is used to calculate the diffusion coefficient value. Figure 2 shows the MSD graph for C6 and C8 molecules at five different concentrations. From the MSD, the diffusion coefficient value was calculated by using the Einstein diffusion Eq. (9) and Eq. (10) below [34,35].

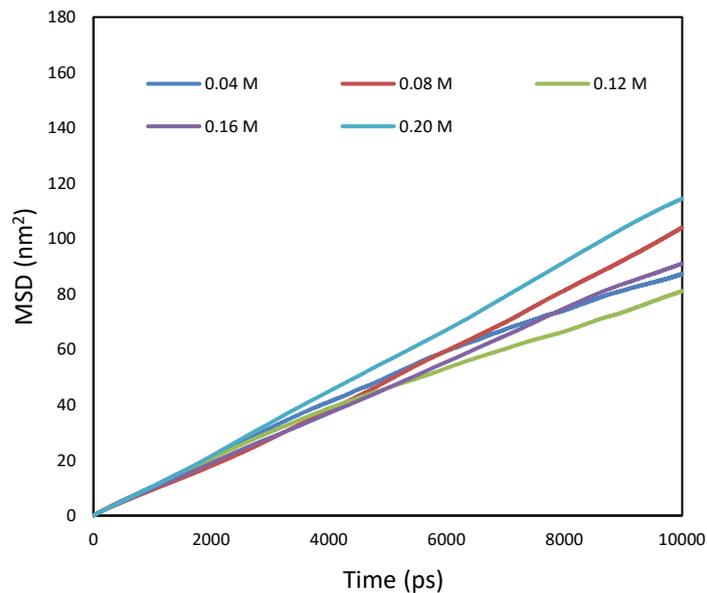
$$MSD = \{[R_i(t) - R_i(0)]^2\} \tag{9}$$

$$D = \frac{1}{6N_a} \sum_{i=1}^{N_a} \{[R_i(t) - R_i(0)]^2\} \tag{10}$$

where  $t$  is time,  $R_i(t)$  is the position vector of a molecule at time  $t$ , and  $N$  is the amount of diffusion molecules. The mean square displacement was derived from the MD simulation, and the limiting slope of the MSD as a function of time can be used to explain the diffusion coefficient of a molecule [36]. The calculated diffusion coefficient value is presented in Figure 3, showing a variation of diffusion coefficient value from a low to a high concentration for molecule C6. At a low concentration (0.04 M), the diffusion towards corrosion particles is low and reaches its highest as the concentration increase to 0.08 M. On the other hand, C8 surfactant shows that the concentration does not significantly affect its diffusion towards corrosion particles where the diffusion coefficient value is low at all concentrations. In the case of corrosion inhibitors, the principal is to form a preventive layer of CI molecules on the metal surface to reduce its corrosion. So, the CI molecules that have a higher diffusion towards the corrosion particles will disturb the main purpose of a CI molecule, which is to be adsorbed on the metal surface. Hu *et al.*, have proved these states where the CI molecules with a higher diffusion coefficient towards the corrosion particle will have a lower inhibition efficiency [36]. The molecular aggregation behaviour of C6 and C8 molecules in different concentrations in the presence of 1 M HCl and 500 ppm acetic acid solution was also observed and tabulated in Table 3. According to Sharma *et al.*, [37], the CI molecules forming a cluster of aggregation will have low adsorption towards the metal surface compared to the CI molecules randomly scattered in the corrosion system. From Table 3, it is observed that the C6 and C8 molecules are randomly scattered in the corrosion system, indicating the ability of these quaternary ammonium cationic surfactant CI molecules to work as a corrosion inhibitor.

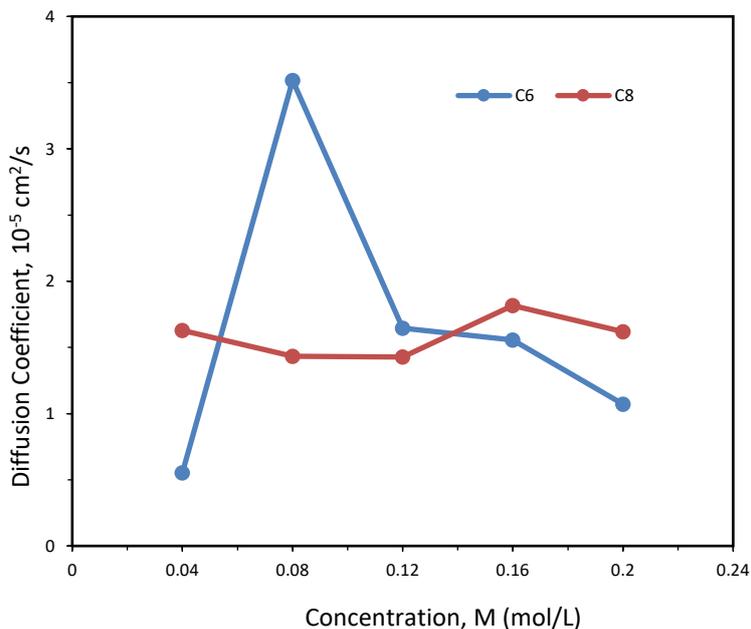


(a)



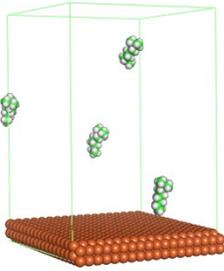
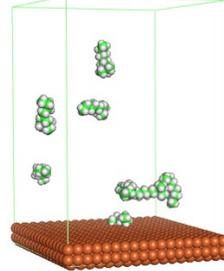
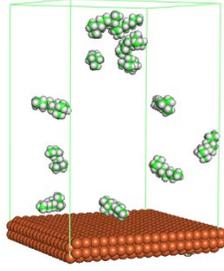
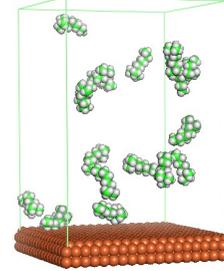
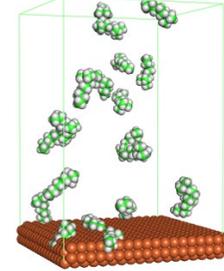
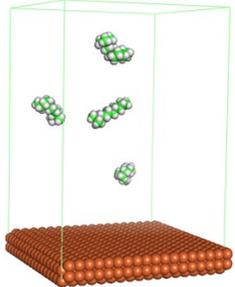
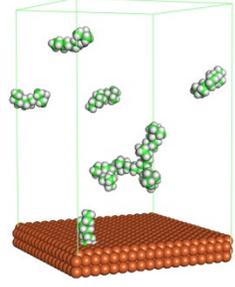
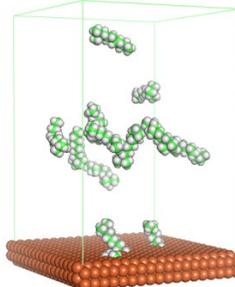
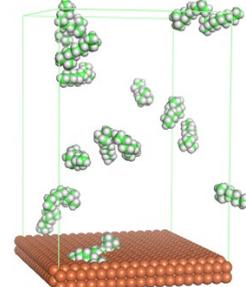
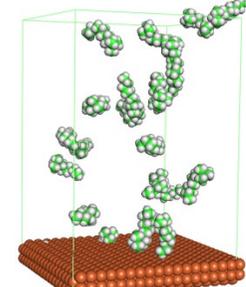
(b)

**Fig. 2.** MSD of (a) C6 and (b) C8 Cl molecules in different concentrations with the presence of 1 M HCl and 500 ppm acetic acid at temperature 333 K calculated via MD simulation



**Fig. 3.** Diffusion coefficient of Cl molecules in different concentrations with the presence of 1 M HCl and 500 ppm acetic acid at temperature 333 K calculated via MD simulation

**Table 3**  
Cluster aggregation of C6 and C8 Cl molecules at different concentrations

Cl Molecule	Cluster Aggregation				
	0.04 M	0.08 M	0.12 M	0.16 M	0.20 M
C6					
C8					

## 4. Conclusions

The theoretical understanding of the mechanism of quaternary ammonium cationic surfactant CI molecules, C6 and C8, are successfully studied by DFT calculation and MD simulation. DFT calculation reveals that the C8 molecule with a longer alkyl chain length has a higher tendency to be adsorbed towards the metal surface with slightly higher HOMO and LUMO energy values than the C6 CI molecule with a shorter alkyl chain length. The HOMO and LUMO, or the reactive region of the CI molecules, are distributed at the positively charged nitrogen ion ( $N^+$ ), and the carbon next to the nitrogen atom represents the importance of these regions for the CI molecules to be adsorbed towards the metal surface. The alkyl chain length does not affect the reactivity of the molecules with the same bandgap energy value (1.26 eV) calculated by the DFT calculation. In MD simulation, the C8 CI molecule was assumed to have a better inhibition efficiency with a higher negative adsorption energy value in the presence of 1 M HCl and 500 ppm acetic acid solution. MD simulation also studied the diffusion coefficient and the molecular aggregation of the CI molecules to understand the CI behaviour in the presence of the corrosion particles. So, the success of DFT calculation and MD simulation in investigating the CI adsorption properties in the presence of 1 M HCl and 500 ppm acetic acid solutions is intriguing for developing new CI molecules with a quaternary ammonium cationic surfactant as basic molecules. The plan for the future endeavour for the CIs development will be to vary the alkyl chain length and branch, with the addition of another functional group. The single CI surfactant can also be compared with its Gemini structure by adding different spacer types.

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