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# 2D-silica ring interactions with alpha olefin sulphonate (AOS) surfactant under AOS/water system using molecular dynamic simulation

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## Abstract

Molecular dynamic simulation of 2D silica and modified silica ring interaction with water/ alpha olefin sulfonate (AOS) was conducted and the interfacial tension as well as diffusion coefficient was predicted through the analysis. The simulation was performed using Material Studio software by assuming the silica nanoparticles as a 2D structure that represents a ring-like shape. The modified 2D silica ring was attached to hexyl-trimethoxysilane (HTMS) to create more hydrophobic structure on the silica surface. The analysis of the mean square displacement (MSD) shows that the diffusion of AOS molecules in the system with modified 2D silica ring were higher than unmodified silica ring which were 0.3099 $\text{Å}^2$/ps and 0.2891 $\text{Å}^2$/ps, respectively. The surface tension for the system after 100 ps with modified 2D silica ring was also lower than surface tension for unmodified silica ring which were $1.80 \times 10^{10}$ GPa and $2.39 \times 10^{10}$ GPa, respectively.

## Article Info

## 1.0 Introduction

Enhanced oil recovery is the tertiary recovery technique employed to extract oil that remains in the reservoir after the first and second recovery technique. This technique can recover up to 60% of oil compared to the 20-40% recovery using conventional method (Tengku Mohd et al., 2016). Gas injection i.e $CO_2$, $N_2$, hydrocarbon gases and air are usually conducted to displace oil and increase the oil recovery. However, fingering phenomena usually occurs due to the low viscosity and density of gas leading to the poor performance of sweep efficiency. Hence foams are used to counter this problem (Wang et al., 2017). To prevent fingering phenomena from occurring, the gas is usually injected together with surfactant in order to produce foam. The stability of the foam is important in the process especially when in contact with oil that can weaken the foam (Wang et al., 2017). Surfactant usually consists of a polar head and a polar tail in its molecular structure. Polar head is hydrophilic, and a polar tail is hydrophobic. These characteristics play an important role as it will help in oil detachment process from rocks or pores. The surfactants reduce the surface tension between oil and water and hence reduces the capillary pressure required to displace the oil from small pores (Emegwalu, 2009). Alpha olefin sulfonate (AOS) has

been reported to be a good foamer (Wang et al., 2017) and it has high compatibility in hard water, as well as having good wetting properties. The drawback of applying this method is that the foam is usually not stable for large scale application, and it is easily collapsed due to extreme reservoir conditions (Kherznejad et al., 2014). The application of nanoparticles has been an interest of many researchers recently for foam stabilization (Horozov, 2008, Binks, 2002, Tengku Mohd et al., 2014, Tengku Mohd et al., 2015) due to its added advantage of being more economical (Bikerman, 1953). Tengku Mohd et al. (2018) studied the $CO_2$ foam stability at various concentration of surfactant, silica nanoparticles and brine solution and it was found that the stability of $CO_2$ foam differs in different concentration of surfactant and silica nanoparticles. However, it was clear in the study that the foams were more stabilized and harder to collapse in the presence of silica nanoparticles. A study by Yousef and Jafari (2015) reveals that silica nanoparticles have the ability to increase the oil recovery by increasing the viscosity of the injected fluid and change the wettability of the porous media to water-wet or partially water wet. Zargartalebi et al. (2015) also investigated the effect of silica nanoparticles and slightly hydrophobic silica nanoparticles where the silica undergoes surface modification to improve the oil

recovery. From the data reported, it shows that with the addition of silica nanoparticles, the surfactant performance efficiency improved and consequently enhancing the oil recovery by reducing the surface tension. However, the use of modified silica nanoparticles proved to further reduce the interfacial value and hence the oil recovery.

This study is focusing on the interaction of water/surfactant/silica ring and water/surfactant/modified silica ring without the addition of oil molecules into the mix. Oil molecules are not considered in this study because only the early stages of the foam stability prior to contact with oil are to be investigated by looking into the surface tension. Long term foam stability is related to the stability of the single foam film where it is used to study the interactions between interfaces (Farajzadeh et al., 2008). Thus, it is important to study the basic properties of the foam film separating the different phases. In oil industry, experimental studies and simulations were implemented in the approach to find a way to improve the oil recovery. However, experimental approach sometimes has proven to be quite difficult to be conducted especially in extreme condition. Hence molecular dynamic modelling is a much preferable way to be used in the investigation and it has been increasingly used in EOR approach (Liu et al., 2015). Molecular dynamics is a powerful tool to study the dynamic behaviour of substance. Furthermore, it is a powerful technique that can obtain thermodynamic properties of the simulate system of given composition at desired pressure and temperature and enable us to investigate microscopic phenomena by direct visualization (Makimura et al., 2013). To date, there is no documented study on the behaviour of silica ring and silica ring modification with hexyl-trimethoxysilane (HTMS) on the AOS/water system using molecular modelling which is the main focus in this study. Hence, it has become the main objective of this study to investigate the effect of silica and modified silica ring on the AOS/water system using molecular dynamic simulation. The properties of the system are to be investigated by looking at the surface tension and diffusion coefficient. Through dynamic simulation, the most suitable condition for the application of EOR can be determined and applied in real life situation.

## 2.0 Methodology

The simulations were performed using Material Studio software version 4.4 from Accelrys. The force field involved throughout the simulation was Condensed-Phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force field (Kim et al., 2016, Sun et al., 2016, Liu et al., 2012, Md Azmi et al., 2019). The calculation for COMPASS force field includes the bonded potential functions such as bond stretching, angular bending, dihedral angle torsion, out of plane interactions and cross terms and the non-bonded van Der Waals and electrostatic interactions (Liu et al., 2016). COMPASS forcefield also can predict the structural and properties of a broad range of organic and inorganic materials including oil, $CO_2$ and water accurately (Sun et al., 1998, de Lara et al., 2012).

The structure of the molecules was constructed using the tools available in the material visualizer. All initial molecule configurations were optimized, and the energy were minimized using geometry optimization. The optimized molecular structure of water, 2D silica ring, 2D modified silica ring (silica ring attached with hexyl-trimethoxysilane (HTMS) molecules) and alpha olefin sulfonate (AOS) was shown in Fig. 1. AOS was built using 14 carbon chain as depicted by Wang et al. (2017).

A system containing water, AOS and silica ring or modified silica ring was constructed using amorphous cell module. Several systems were constructed with constant number of water and AOS molecules but with different number of 2D-silica rings (Table 1). The 2D-modified silica ring system used the same amount of water and surfactant i.e. 1200 and 20, respectively but only 5 molecules of 2D-modified silica ring were added in the construction. The total percentages of HTMS molecules attachment to the 2D-silica ring were varied at 20, 40, 60 and 80% which correspond to 9, 23, 52 and 137number of HTMS, respectively. The construction of HTMS attachment to silica ring was modelled based on the general attachment of silane on ceramic surface as shown in Jayasuria et al. (2017).

After construction, all systems were refined by subjecting the systems to geometry optimization to optimize the molecular arrangement and minimize the energy. The systems were further refined via short dynamic simulation before it was subjected to the production run using dynamic simulation (Liu et al., 2016) for 100 ps using dynamic simulation. Dynamic simulation was conducted with NPT (constant number of molecules, constant pressure, constant temperature) ensemble (Liu et al., 2015) where the pressure and temperature were controlled using Berendsen barostat and thermostat, respectively.

The temperature was set to 298K and the pressure was at 1 atm. The time step used was 1 fs with trajectory
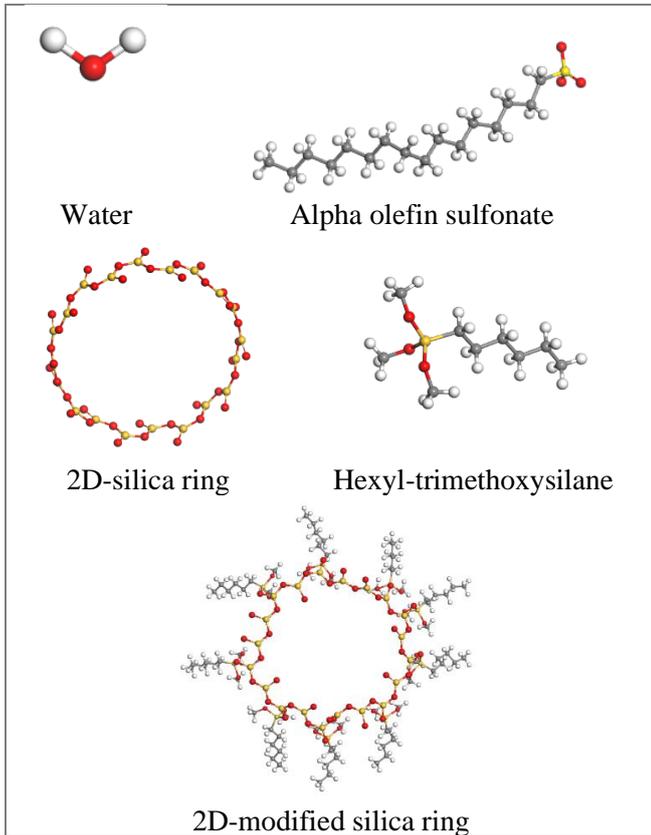
**Fig. 1**: Molecular structure of water, alpha olefin sulfonate (AOS), 2D-silica ring, hexyl-trimethoxysilane (HTMS) and 2D-modified silica ring.

**Table 1**: The number of water, AOS and silica ring in each system constructed.

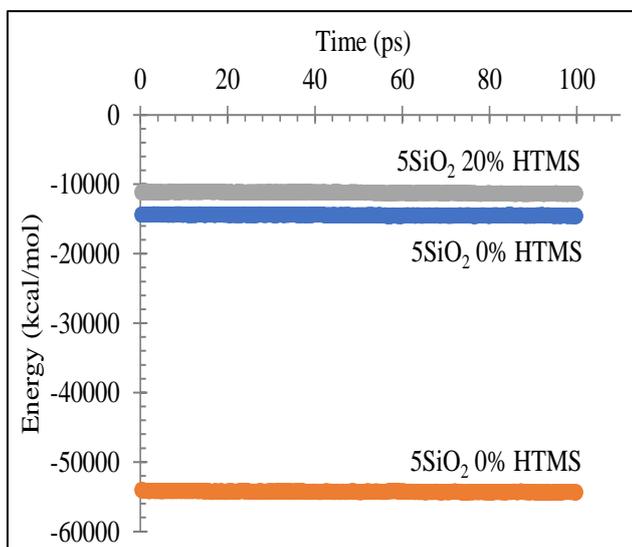| Systems | Number of molecules | | |
|---------|-------|------|------------|
|         | Water | AOS  | Silica ring |
| S5      | 1200  | 20   | 5          |
| S10     | 1200  | 20   | 10         |
| S15     | 1200  | 20   | 15         |
| S20     | 1200  | 20   | 20         |
| Control | 1200  | 20   | 0          |



**Fig. 2**: Total energy of different systems during dynamic simulation for 100 ps showing a stable condition.

of the result was recorded for every 1000 step. The trajectory of the result was analysed and the means square displacement (MSD) curve vs $t$ (time) was obtained. The MSD curve was related to the diffusion coefficient of AOS through Einstein relation portrayed in Eq. (1) where the slope of the MSD vs $t$ was used to calculate the diffusion coefficient. $r_i(0)$ and $r_i(t)$ stands for the coordinates of particle $i$ at initial and time $t$ respectively and $<[r_i(t) - r_i(0)]^2>$ is the mean squared displacement of coordinates (de Lara et al., 2012, Zeng et al., 2013).

$$D = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \langle |r_i(t) - r_i(0)|^2 \rangle \tag{1}$$

Meanwhile, the cohesive energy density (CeD) analysis was conducted and the data was used to calculate the surface tension, $\gamma$ of the system using Eq. (2) where $V$ is the molar volume of the mixture (Aqra, 2014);

$$CeD = 16.8 \left( \frac{\gamma}{V^{1/3}} \right)^{0.86} \tag{2}$$

## 3.0  Results and discussion

To obtain an accurate result for molecular modelling, it is important for the simulated system/cell to reach equilibrium before the analysis of its properties can be conducted. The equilibrium of the system was determined by the energy profile extracted from the simulation data where the acceptable fluctuations of the energy and temperature data were in the range of 5–10% (Zeng et al., 2012).

Fig. 2 shows the energy profile of three different model systems. From the result obtained, it can be seen that the system was in an equilibrated state and stable with barely any fluctuations observed. This also shows that the duration of the dynamic simulation time 100 ps is sufficient for this system. Fig. 3 shows the trajectory of the molecules as the dynamic simulation time increased. The molecules were coloured green for water, blue for alpha olefin sulfonate, while the silica ring and modified silica ring with hexyl-trimethoxysilane molecules are in their original colour where red is for oxygen, grey for carbon and yellow for silica. At 20 ps, molecular structuring was observed in the system compared to the system at the initial state, 0 ps. As the time increased, the mobility of the molecules increased as observed in 50 ps and 100 ps. The molecules are more dispersed as the dynamic simulation progressed.
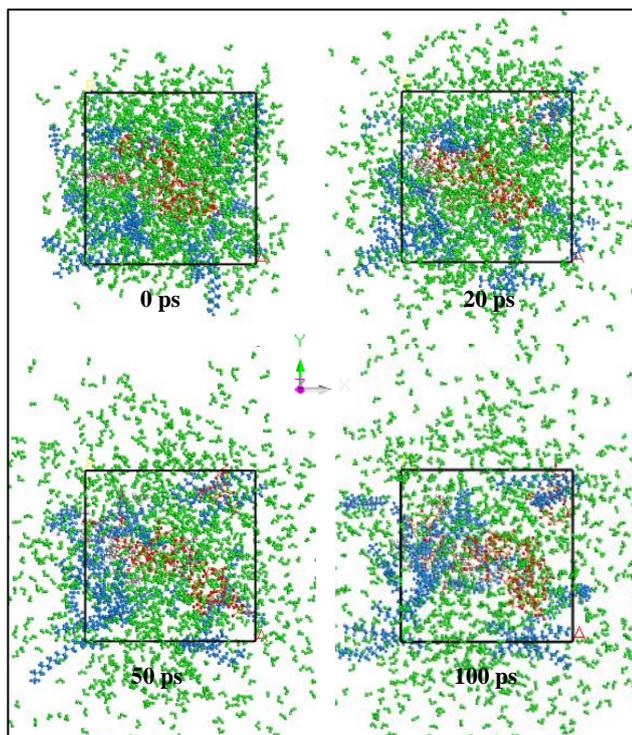
**Fig. 3**: Mobility of the molecules in the model system with 5 number of 2D-modified silica ring and 20% HTMS. Colour code: green for water, blue for alpha olefin sulfonate, red is for oxygen, grey for carbon and yellow for silica.
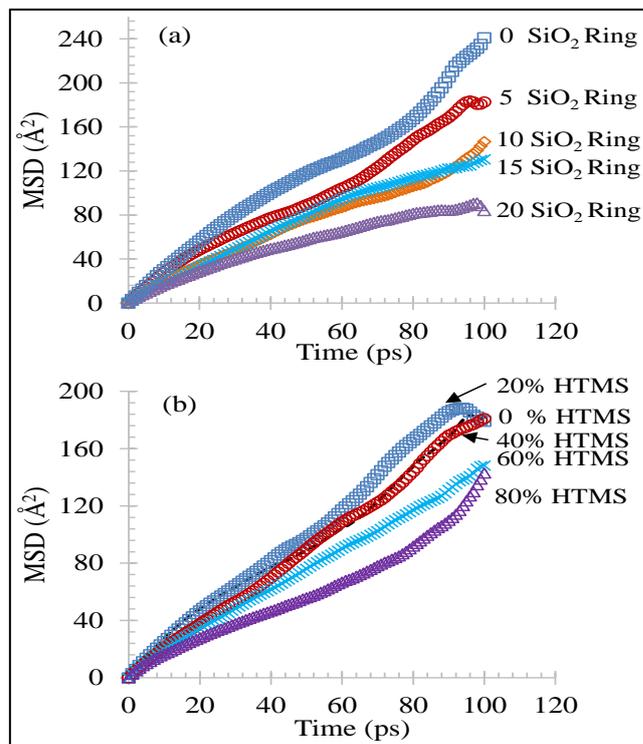


**Fig. 4**: Mean square displacement (MSD) of water/ AOS system containing (a) different amount of silica ring and (a) 5 number of 2D-modified silica ring with different amount of HTMS attachment.

Fig. 4 shows the mean square displacement (MSD) of water/surfactant (AOS) system containing different amount of unmodified 2D-silica ring and 5 number of modified 2D-silica ring with different amount of HTMS molecules. Fig. 4a shows the addition of unmodified 2D-silica ring reduced the diffusion of AOS due to the increase number of molecules in the system. The addition of molecules in the system restricts the mobility/movement at the boundary of the macromolecules (Makarov et al., 1998). In this case, the addition of unmodified 2D-silica ring restricts the mobility of AOS molecules when the 2D-silica ring obstructs the AOS from moving freely in the system when they are in contact with each other. Too much amount of adding 2D-silica ring disturbed the water/AOS system as shown in Fig. 4a, due to the reduction in the dimensionality of available space in the system for the particle to be mobile when more large molecules are added in the system (Makarov et al., 1998). The trend of the mobility of AOS in the presence of 5 number of 2D-silica ring (S5) was the highest amongst the system having the 2D silica ring. The S5 system increased gradually with time which finally showed MSD of 180 $\text{Å}^2$.

The larger slope of the MSD curve reflected higher chain mobility of AOS (Makimura et al., 2013) whereby

it indicates the ability of diffusion of AOS molecules into the system. Thus, 5 number of unmodified 2D-silica ring was the best condition (Fig. 4a) and was selected for creating modified 2D-silica whereby certain amount of HTMS was introduced (Fig. 4b).

By attaching the HTMS molecules which created more hydrophobic surface on the 2D-silica ring, the diffusion coefficient of AOS also reduced significantly except for 20 and 40% attachment due to the interaction of AOS and modified 2D silica ring.

It is reported by Su et al.(2010) that attractive interaction of a molecule with another lead to a reduction in the mobility. The addition of HTMS that created more hydrophobic structure and discouraged the diffusion of AOS because AOS molecules interacted with the 2D silica ring. Since AOS also possess a long hydrocarbon chain which is hydrophobic, it is easily attracted to the hydrophobic structure of HTMS protruding outward from the 2D silica ring. Hydrophobic molecules tend to interact with each other to avoid water molecules (Florence and Attwood, 2006) and interaction of these two molecules reduced the AOS diffusion coefficient (Su et al., 2010) since the mobility of AOS was restricted due to the interaction.

Fig. 5 shows the diffusion coefficient of AOS that was calculated using Eq. (1). The diffusion coefficient
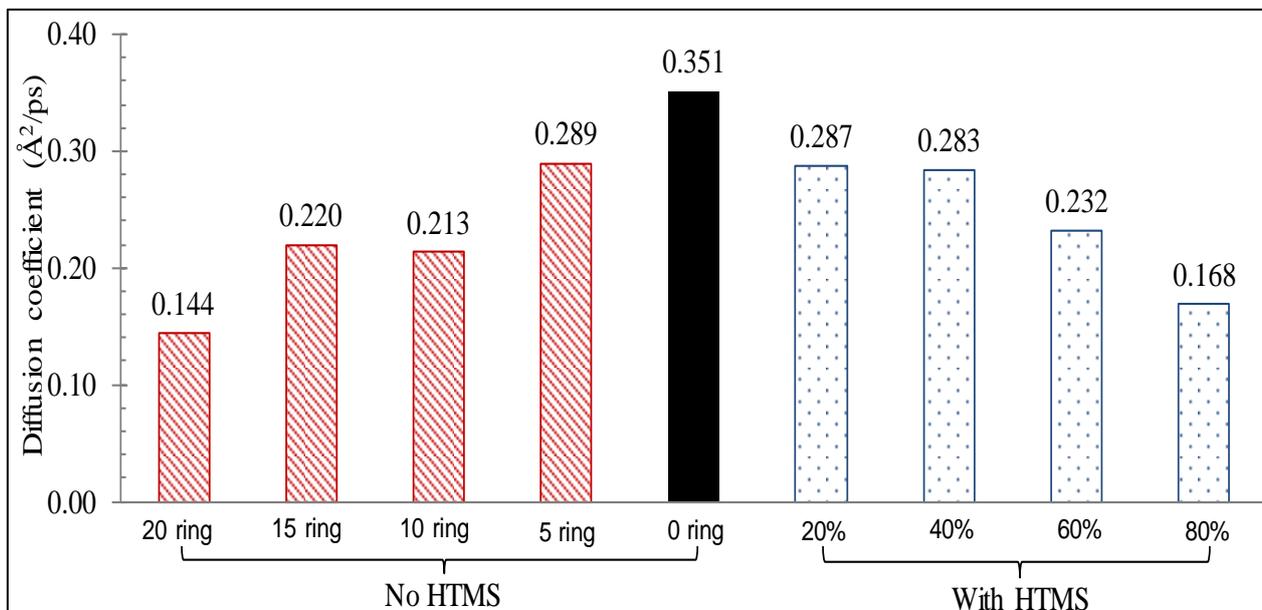
**Fig. 5**: Predicted diffusion coefficient data of AOS molecules in the system with different number of unmodified 2D-silica ring (striped), system without silica ring (black) and 5 modified 2D-silica rings with different number of HTMS attachment (dotted).

was also the highest when there was no 2D-silica ring in the system with the value of 0.351 $Å^2$/ps showing that less molecules in the system indeed helps in the mobility of AOS molecules. The system with unmodified 2D-silica rings showed that increasing the number of silica rings reduced the diffusion of AOS molecules to 0.144 $Å^2$/ps. The effect of introducing modified 2D-silica ring to the system shows that with the increment of HTMS attachment onto the 2D-silica ring, the diffusion coefficient reduced from 0.351 to 0.168 $Å^2$/ps. Similar trends of the AOS diffusion coefficients were in agreement with the MSD results in water/ AOS system for the unmodified and modified 2D-silica ring due to the same behaviour of interactions as explain previously (cf. Fig. 4).

Fig. 6 shows the calculated surface tension value of the system with unmodified and modified 2D-silica rings. Based on cohesive energy density (CeD) data that can be obtained from the forcite in the simulation, surface tension can be calculated using Eq. (2). Surface tension is proportional to the CeD whereby it characterises the strength in the physical quantity of the interactive force among molecules of a substance (Aqra, 2014). Among the unmodified silica ring system, only 5 number of 2D-silica ring maintains the same value of surface tension as the control system (water/ AOS only). The addition of more than 5 unmodified 2D-silica ring increased the surface tension of the system. AOS is a surfactant commonly used to reduce the surface tension of water (Hu et al. 2016). However, the addition of 2D-silica ring disturbed the function of surfactant in the water/ AOS system. On the other hand, the system with

modified 2D-silica ring showed that the surface tension reduced when the attachment of HTMS molecules onto the surface of silica ring increased where the lowest surface tension was at 80% of HTMS attachment.

This may be due to the hydrophobicity of the modified 2D silica ring that contribute to the reduce value of surface tension. The reducing of the surface tension occurs when the hydrocarbon tail of surfactant With the increase amount of HTMS concentration on the surface of 2D silica ring, it became more hydrophobic.

There is a possibility for the modified 2D silica ring to orient themselves to the surface of water in order to escape the unfavourable interaction with water in the bulk. Surface properties depend on the hydrophobic chain of a molecule (Xu et al., 2013). Study by Pradines et al. (2010) on different alkyl chain of alkyl trimethylammonium bromides adsorption on water/air and water/hexane surface shows that higher alkyl chain of $C_{12}$ has a lower surface tension than $C_{10}$ alkyl chain. This shows that higher hydrophobicity leads to a lower surface tension and hence better recovery of oil.

**4.0 Conclusions**

It can be concluded that the dynamic simulation of water/AOS with silica ring and modified silica ring was successfully conducted. Based on the mean square displacement and diffusion coefficient analysis, the presence of silica ring reduces the mobility of AOS molecules in the system, however the presence of modified silica ring with different attachment of HTMS on the surface does not give a specific trend in the
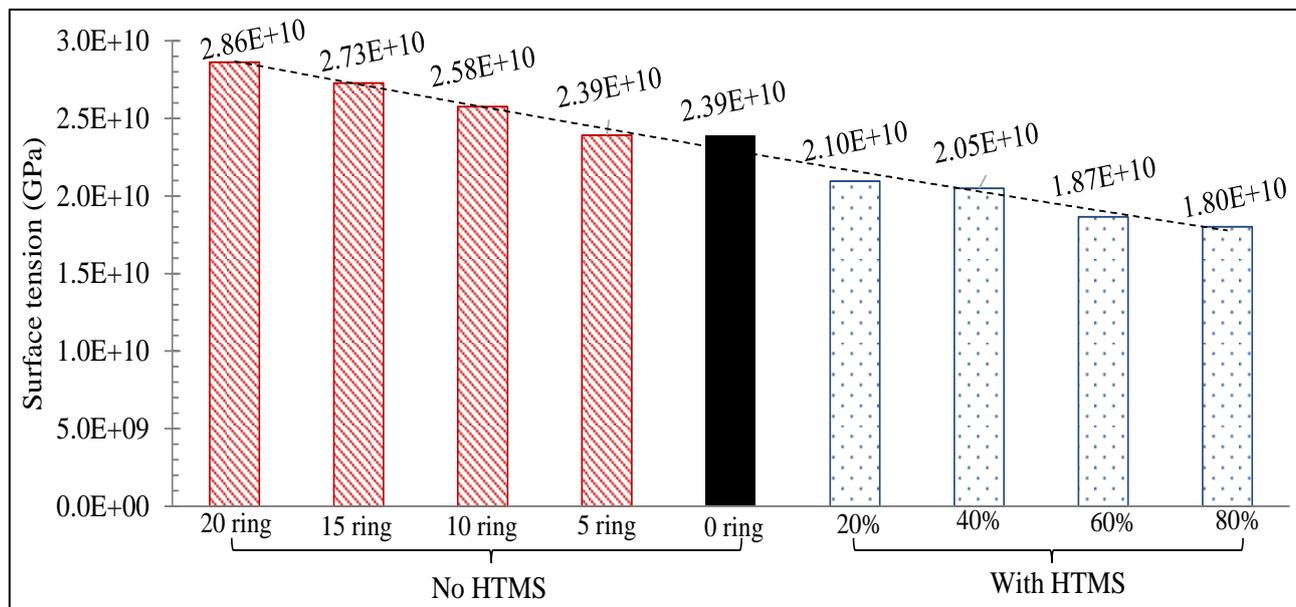
**Fig. 6**: Surface tension of the system in the presence of different number of unmodified 2D-silica ring (striped), the system without any silica ring (black) and 5 modified 2D-silica rings with different amount of HTMS attachment (dotted).

mobility of AOS. However, based on the surface tension predicted from the cohesive energy density (CeD) data, it was shown that the water/AOS system with the presence of modified silica ring gives a lower surface tension than the system with unmodified silica ring. Higher attachment of HTMS molecules for the modified silica ring also reduces the surface tension where the 80% HTMS attachment gives the lowest surface tension, hence better chances for the recovery process in EOR technique. Since only 2-dimensional configuration of silica surface was used in this simulation, it is recommended to simulate the system with spherical nanoparticles to see the effect on the water/surfactant system.

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