Surfactant-Water-Modified Silica Nanoparticle Molecular Interactions

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***Abstract* — The involvement of Nano Technology and silica in the foam formation plays an important role to enhance the oil recovery. However, its molecular dynamic interface abilities and interactions behavior were not widely known. The challenge in the foam flooding was foam created was easy to break. It was difficult to maintain the stability of foam created when comes in contact in the reservoir due to the lower of viscosity effect. Thus, the molecular interactions behaviors and understanding the structural and dynamic information of the adsorption of Alpha Olefin Sulfonate (AOS) on the interface of water and air was conducted using molecular dynamic simulations. The modification of silica nanoparticles (SNP) demonstrated by attachment of Hexyl-trimethoxysilane (HTMS) on SNP surface. From the simulation, the data such as Mean Square Displacement (MSD) and Cohesive Energy Density (CED) were extracted as measurement to investigate the diffusivity and water-air surface tension, respectively. The diffusivity of AOS in the system that using modified SNP was higher than SNP without HTMS which was 0.3099 $Å^2$/ps and 0.2891 $Å^2$/ps, respectively. In addition, the surface tension for the system with HTMS was lower than surface tension for SNP without HTMS which was $1.80x10^{10}$ GPa and $2.39x10^{10}$ GPa, respectively after 100 ps. These result indicated that the modified SNP with HTMS improved the adsorption of the surfactant. Thus, the foam stability was slightly higher with the presence of HTMS on SNP surface.**

Keywords— Enhanced Oil Recovery (EOR), Surfactant Flooding, Silica Nanoparticles, Hexyl-trimethoxysilane, Alpha Olefin Sulfonate, Molecular Dynamics,

I. INTRODUCTION

Crude oil from reservoirs that left after primary and secondary oil recovery contains about two-third of the original oil in place. The high capillary pressure from water in the reservoir's pores traps much of the original oil. Enhanced Oil Recovery (EOR) or tertiary recovery was introduced to improve the efficiency of oil recovery in the reservoir up to 60% recovery. The foam flooding were one of the alternatives that was used in Enhance Oil Recovery (EOR) which was by using surfactant to achieve high sweep and efficiency to recover the left quantity of oil in the reservoir. However, the main challenge when using foam was to maintain the long term stability of the foam. This is due to the lower viscosity that leads to the reduction of efficiency of oil recovery and due to extreme reservoir conditions as well as high loss-rate of surfactant during the process [13]. It is challenging as high salinity and high temperature limiting the performance of foam in the reservoir [14].

Many researchers have recently investigated addition of nanoparticles into the injected surfactant flooding to EOR. Mostly of the research were covered the main concern regarding the challenges of the surfactant itself in EOR such as interfacial tension reduction, viscosity reduction, wettability alteration, enhancing of thermal conductivity and oil transportation in long distance of reservoir with nanoparticles stabilized emulsions [13]. Recent work by Yousefvand and Jafari (2015) revealed that nano particles were able to change the water-wet from wettability [28].

In petroleum recovery, the important part that has been considered was the physical properties of the interface. The presence of surfactant created better surfaces activity on the particles that dissolve. The application of surfactant was quite famous in petroleum recovery. In addition, surfactant also being use in processing industry, oilwell drilling, reservoir injection, oilwell production, surface plant process, pipeline and seagoing transportation of petroleum emulsions [37]. The wetting agents contains in surfactant caused the interfacial tension between oil and water to decrease, allowed it to overcome the high capillary pressure required to move oil out of very small pores [4]. Among the many types of surfactants, alpha olefin sulfonate (AOS) surfactant was figured out as a good candidate in this surfactant flooding in EOR due to its high compatibility in hard water, high detergency capability and good wetting and foaming properties [13].

This study was conducted in demonstrating the usage of SNP to enhance the oil recovery and the effect of addition HTMS to the surface of SNP. The SNP was built into ring shape with 20 molecules of silica dioxide. Then, the SNP was interacted in system contains water and AOS. Those interactions were performed by using the Material Studio 7.0 from Accelrys, Inc. The Molecular Dynamics Simulations (MDS) provided the understanding at molecular level through the behavior of surfactant-water-silica nanoparticle interactions, structural condition and dynamic information of the adsorption process. The SNP was modified by attachment of HTMS. The modified silica was created in nanoparticles form and was assumed to be in 2D structure due to some limitations in Material Studio 7. The strength of the created foam was studied using Material Studio 7. The strength and the effect of the amount of HTMS added to the SNP can be investigated by conducted the modeling.

The aim of this study was to develop the molecular model between modified SNP, AOS, HTMS and water in order to investigate the molecular interaction behavior and ability of AOS, SNP, water and HTMS for stabilization of foam. Thus, the effects of the addition HTMS on the surface of SNP toward AOS behavior and foam stability can be identified.

II. METHODOLOGY

A. Modeling Simulation

The simulations were performed by using software named Material Studio 7.0 from Accelrys, Inc. The simulations were performed using Material Studio 7.0 by Accelrys, Inc. Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) was applied to all the potential parameters. The COMPASS validity was guaranteed as the calculated vibration frequencies, molecular structure, crystal cell parameters and density, conformational properties for isolated molecules, heat of evaporation and liquid density agreed favorably with most experimental data [23].

The molecular structures for water, AOS, SNP or SiO_2 and HTMS were constructed together with atom's charges. The single molecule SiO_2 was used to construct SNP which was assumed to be in two dimensions (2D) ring structure because of the interaction only occurs at the outer surface of SNP. This was made to ease to observation for the interaction that occur at the surface of SNP. The best amount of SiO_2 molecule that gave the highest diffusivity and lowest surface tension are 100 molecules. Therefore, one ring of 2D SiO_2 consisted of 20 molecule of SiO_2. The modification of the 2D SiO_2 was constructed by the attachment of HTMS. The HTMS molecule was manually attached to 2D SiO_2 with percentage attachment of 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80% and 90% to 100 molecule of SiO_2. Then, the structure was optimized. The optimization was done using forcite module. Table 1 showed the parameters that were used under *energy tab* in forcite calculation to optimize the structure.

Table 1: Optimization parameters

Forcefield	COMPASS II
Charges	Use current

COMPASS II was the upgraded forcefield in the material studio 7. This gave more accurate result than the other forcefield. In order to ensure the charges for every atom in the structure were not disappeared after the optimization, the *use current* was selected and assigned to the molecule as the charge parameter. When optimization was completed, the system consists of water, AOS and 2D SiO_2 were created using Amorphous Cell module. Table 2 shows the parameters that were used for Amorphous Cell Calculation.

Table 2: Amorphous Cell parameters

Molecule	Loading
H_2O	1200
AOS	20
2D SiO_2 (modified)	5

Table 3: Amorphous Cell Energy Tab

Forcefield	COMPASS II
Charges	Use Current
Electrostatic	Ewald

Ewald in table 3 was chosen because *ewald* summation was the most accurate method for computing the long-range electrostatic interactions [32].

Table 4: Simulation environment with various percentage of attachment HTMS

Systems	HTMS Attachment to 100 molecule SiO_2 (%)	Number of molecules	
		Water	Surfactant
S1	10	1200	20
S2	20		
S3	30		
S4	40		
S5	50		
S6	60		
S7	70		
S8	80		
S9	90		

Table 4 shows the number of molecule that was used to construct the various systems using *Amorphous Cell Calculation* module. Then, the systems created were optimized to get the most stable system by using the same parameter as shown in Table 1. After the optimization completed, the short dynamic simulation was executed. *Short dynamics simulation* was conducted to obtain the stable structure in terms of energy before prior to *dynamic simulation.* Table 5 was provided the parameters that were used for the *short dynamic simulation*.

Table 5: Short Dynamics parameter of the simulation

Time step	1 fs
Ensemble	NPT
Temperature	298 K
Pressure	0.0001 GPa
Number of steps	10000
Duration	10 ps

NPT means that the system was control by pressure and temperature. When the *short dynamic* completed and the system was stable, the *dynamic simulation* was set up with the parameter as shown in Table 6.

Table 6: Dynamics parameter of the simulation

Time step	1 fs
Ensemble	NPT
Temperature	298 K
Pressure	0.0001 GPa
Number of steps	100000
Duration	100 ps

B. Model analyses and property calculations

Forcite analysis module was used to generate data of MSD. The MSD data obtained was used to calculate the diffusivities (D) by using Einstein equation [5, 13, 15, 16] as in Equation (1):

$$D = \frac{1}{6}\lim_{t\to\infty}\frac{d}{dt}\langle[r_i(t) - r_i(0)]^2\rangle \quad \text{..... (1)}$$

The $r_i(t)$ and $r_i(0)$ in the Equation (1) are the position vector of atom R at time t and 0 respectively. While $\langle[r_i(t) - r_i(0)]^2\rangle$, is a Mean-square displacement (MSD) indicates the average of all chosen atoms of time origin in a dynamics trajectory where also used for comparing the motilities of functional groups as well as to calculate diffusivities of protons. Diffusivity also related to the slope of the MSD graph. The steepest the slop, the highest the diffusivity become. In this simulation, diffusivity of AOS are the main interest of the study.

The cohesive energy density (CED) was used to calculate the surface tension between the AOS and water. The CED was generated by using forcite module. Hildebrand and Scott have proposed the relationship which as in Equation (2):

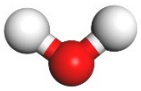
$$CeD = 16.8\left(\frac{\gamma}{V^{1/3}}\right)^{0.86} \quad \text{..... (2)}$$

The variable V was the molar volume of the mixture. This equation is only suitable for non-associated small molecular systems [1].

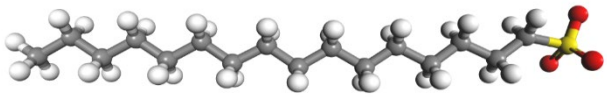
III. RESULTS AND DISCUSSION

A. Construction of molecules

The construction of the molecule must exactly follows the real structure so that the reactions between them will be close as real situation and approximately same as what happen in experiment.



(a)



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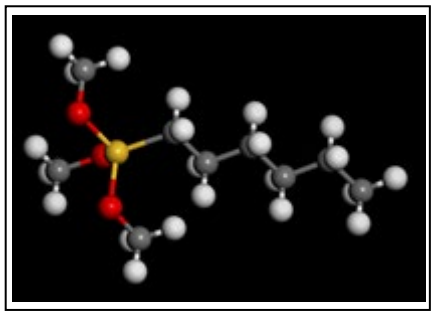

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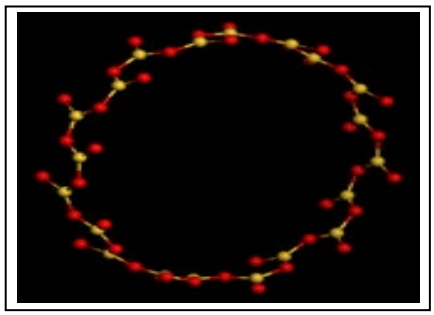

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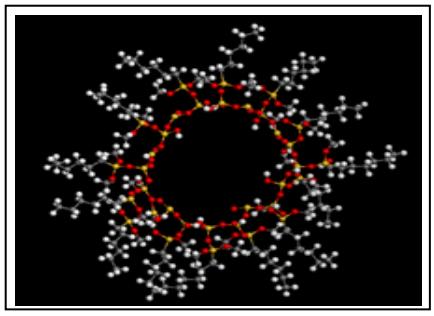

(e)

Figure 1: The optimized structure of the molecules (a) Water; (b) AOS; (c) HTMS; (d) 2D SNP ring; (e) 2D modified SNP ring

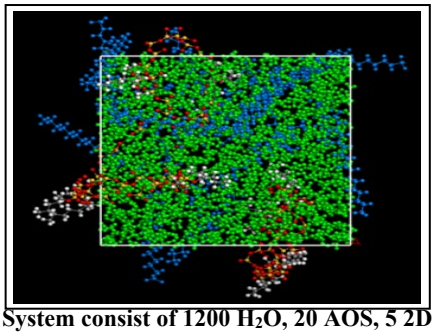

Figure 2: System consist of 1200 H_2O, 20 AOS, 5 2D SNP ring modified by 10% attachment of HTMS (Green: H_2O, Blue: AOS, Others: 2D SNP ring modified by HTMS)

B. AOS surfactant diffusion property into the system with and without HTMS on the surface of the SNP

The addition of SNP was to increase the surface activity of AOS molecules. SNP was interacted with AOS molecules to generate adsorption at solid and liquid interfaces and it was used for stabilization and destabilization of foams. The interaction between SNP and AOS were crucially important.

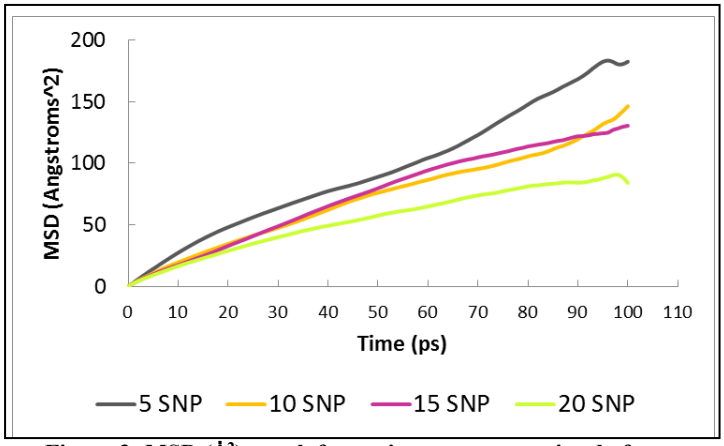

Figure 3: MSD (Å^2) graph for various system consisted of different amount of SNP without HTMS

Figure 3 showed the MSD result for the various systems that consist of number of SNP. The parameter was conducted to study the best amount of SNP that can give the best diffusivity of AOS. By using data from Figure 3, the diffusivity for AOS was calculated using Equation (1). The diffusivity obtained was plotted as shown in Figure 4.

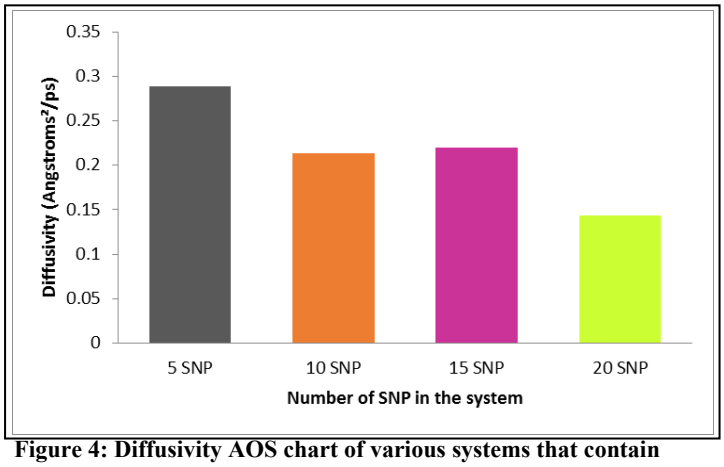

Figure 4: Diffusivity AOS chart of various systems that contain different number of SNP

Based on Figure 4, 5 SNP gave the highest diffusivity of AOS in the system. The other parameter that was observed and calculated was surface tension which has been calculated using Equation 2.

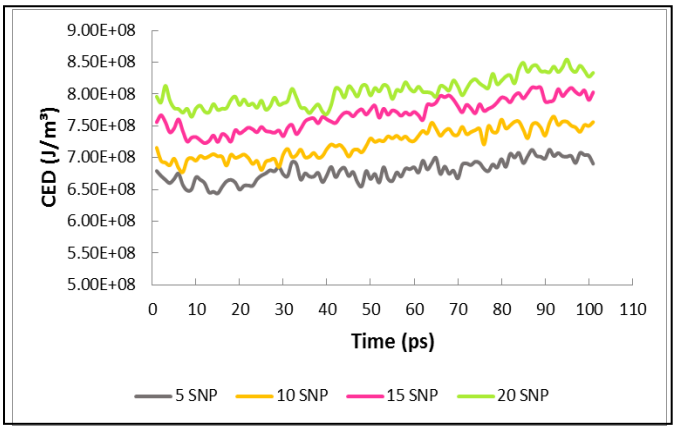

Figure 5: Cohesive Energy Density (CED) data

The data in Figure 5 was extracted using *forcite calculation.* The CED data collected was used in calculating the surface tension using Equation 2. The surface tension obtained was plotted in the Figure 6.

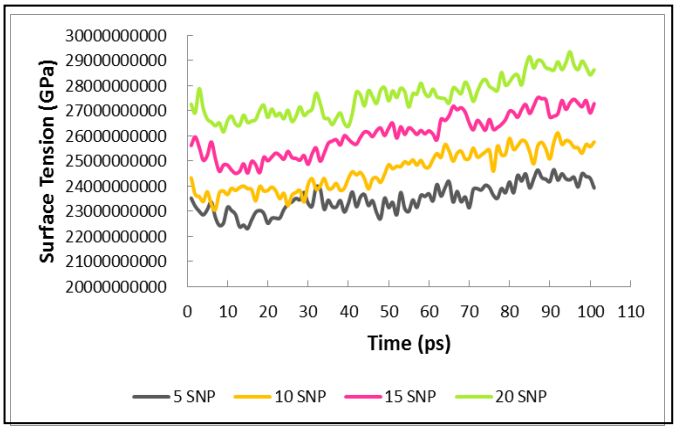

Figure 6: Surface Tension of system without HTMS

Based on Figure 6, the surface tension recorded after 100 ps for 5 SNP, 10 SNP, 15 SNP and 20 SNP were $2.39x10^{10}$ GPa, $2.6x10^{10}$ GPa, $2.7x10^{10}$ GPa and $2.9x10^{10}$ Gpa respectively. Therefore, the surface tension for all system was 20 SNP > 15 SNP > 10 SNP > 5 SNP. 5 SNP gave the lowest surface tension after 100 ps. 5 SNP equivalent to 100 molecule of SiO_2.

The untreated SNP such as hydrophilic silica particles was not surface active at the liquid interface but their presence in a system containing surfactants can strongly affect the surface properties of the solution [33]. The silane coupling agents were one of the commonly used materials for enhancing the mechanical properties of the overall system [34]. Therefore, 5 SNP was selected and used in the next study.

The next study was modified the SNP by attachment of HTMS on its surface. The HTMS was one of the commonly used materials for enhancing the properties of the overall system [31]. This study was conducted to study the effect of addition HTMS on the surface SNP toward AOS behavior, surface tension of the system and foam stability.

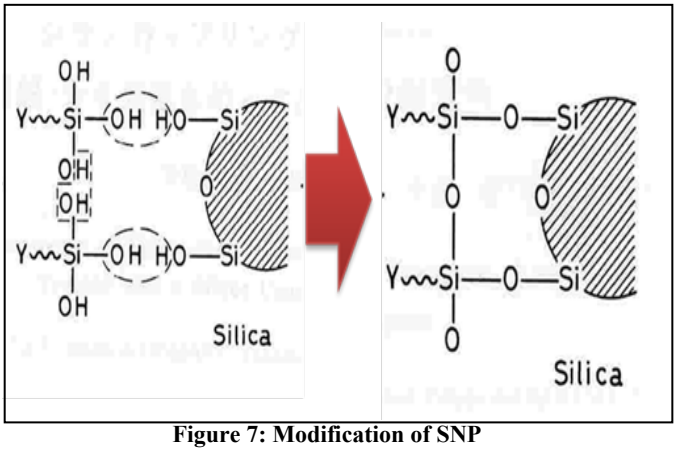

Figure 7: Modification of SNP

Figure 7 showed the modification of the surface of SNP with the attachment of HTMS. The modification was occurred at the surface of SNP. That was the reason why the structure of SNP constructed was assumed in two dimension (2D) ring.

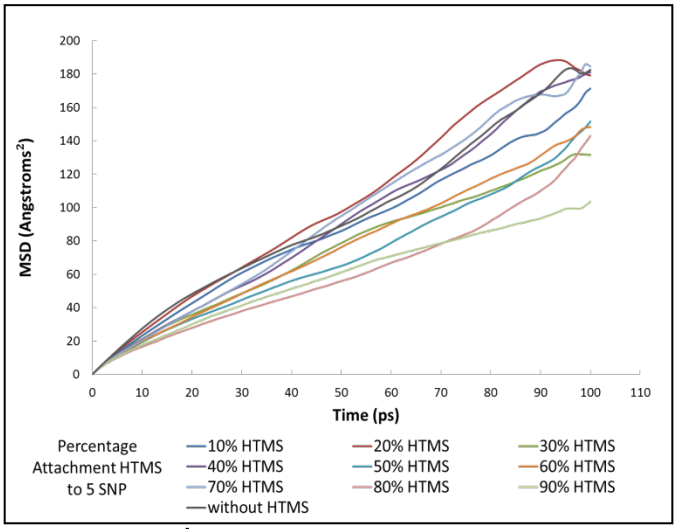

Figure 8: MSD (Å²) graph of system with and without HTMS on ring-shape SNP

The effect of adding HTMS to the foam stability was observed based on the diffusivity of the surfactant. The foam stability mainly depends on the behavior of the surfactant. From MSD of the AOS that was showed in Figure 8, the behavior of AOS with the presence of HTMS was understood. From Figure 8, the slope was identified in order to determine the higher mobility in the system [30]. The diffusivity was calculated using Equation 1.

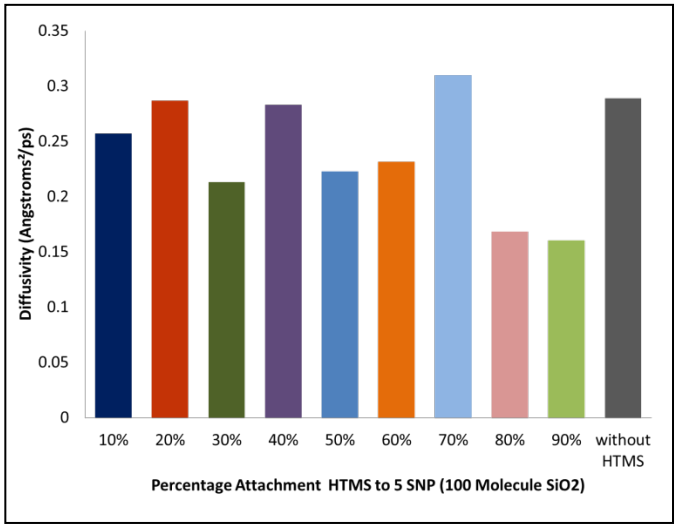

Figure 9: Diffusivity AOS chart of various systems that contain different number of percentage of attachment hexyltrimethoxysilane on ring-shape silica nanoparticle

Based on the results obtained in Figure 9, the percentage of attachment HTMS to 5 SNP (100 molecule SiO2) which was 70% gave the highest diffusivity and highest mobility of AOS in the system. It shows that at this amount of HTMS, the interaction between AOS and modified SNP were good. 70% attachment was equal to 42wt% of the system. This wt% was calculated by considering the mass for the all molecule in the system. From this resulted, it is clearly observed that the amount of HTMS added to SNP in the system affects the AOS diffusivity. The highest addition of HTMS on the surface of SNP caused the reduction in the diffusivity of the AOS in the system.

Foam stability was observed by using surface tension of the system. The higher the maximum rate of surface tension reduction, gave the higher the diffusivity and foaming properties in term of foamability and foam stability [35]. Generally, AOS was used to reduce the surface tension in the system. An important point was to understand the foam behaviors, which are fundamentally governed by the properties of added surfactants including other soluble components present in water especially type and chemical structure [35].

Because of the SNP are hydrophilic group, the modification of its surface was done to make it slightly hydrophobic. Higher hydrophilic head group size result in decrease in surfactant adsorption density, causing the reduction of surface activity and the surface tension equilibrium process comprises diffusion of surfactant molecules between bulk liquid and sub-surface layer, and the transfer of molecules between sub-surface layer and the surface[36]. Thus, fresh surface are created and it make the surface tension higher than the equilibrium value. As the surface ages, the surface tension declines and surfactant diffuses towards the surface and is adsorbed [36].

The larger the volume of the hydrophobic and hydrophilic portions lossen the arrangement of molecule at the interface of air and water. The hydrophobic and hydrophilic portions can affect the surfactant adsorption efficiency. Higher surfactant adsorption efficiency at the air and water interfaces greater ability for the reduction of surface tension.

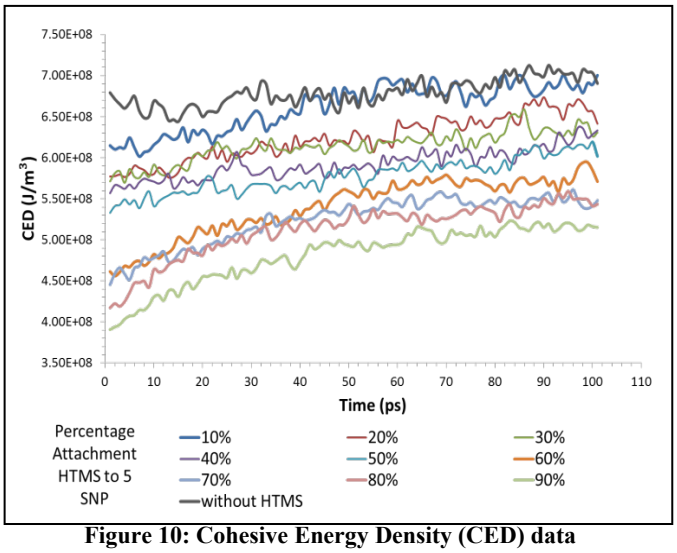

Figure 10: Cohesive Energy Density (CED) data

Figure 10 showed the CED data that was extracted using *forcite calculation module.* The CED data was inserted in Equation 2 in order to calculate the surface tension. The surface tension calculated was plotted as shown in Figure 11.

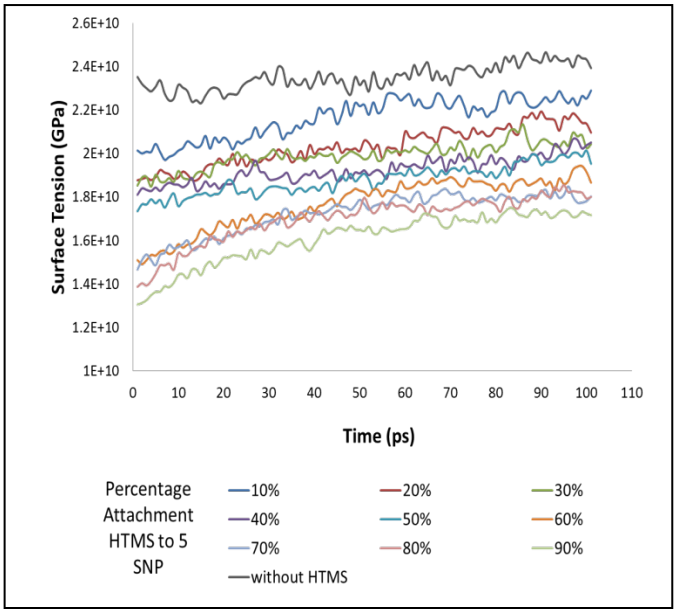

Figure 11: Surface Tension of system

Based on result obtained, the lowest surface tension is 90% of attachment of HTMS to 5 SNP (100 molecules SiO_2). But at this level of surface tension, the diffusivity of the AOS was lower. That was means that the conditions of the modified SNP are having too much hydrophobic portion and it causing an increasing in the aggregation number. It is true that large volume of the hydrophobic and hydrophilic portions, leading to a losser arrangement of molecule at the interface of air and water and greater ability to reduce surface tension. It is obviously can be seen in the graph plotted the 90% of attachment have the highest ability to reduce surface tension and having the lowest surface tension which is 1.72×10^{10} GPa after 100 ps but, the hydrophilic and hydrophobic portion for 90% attachment of HTMS are not suitable. It caused the arrangement at the interface are too losse and lead to the lowest diffusivity of AOS. Besides, the data for CED that was collected is for the overall system. As mention before this, the aim was to losse the arrangement at the interface of air and water or in another word was to reduce the surface tension of air and water so that AOS are easy to diffuse into it.

The diffusivity and surface tension for the system with HTMS were compared with the system without HTMS to see the effect of addition of HTMS. The diffusivity of AOS in the system with 70% of HTMS is higher than diffusivity in system without HTMS which were 0.3099 (Angstroms^2/ps) and 0.2891 (Angstroms^2/ps) respectively. It shows that the addition of HTMS to the structure of SNP was good for foam stability. This happen because SNP without HTMS are hydrophilic. The hydrophilic was not suitable to interact with anionic surfactant. It limited the behavior of AOS and lead to the low diffusivity of AOS in the system.

From Figure 11, it clearly observed that the surface tension after 100 ps for system with 70% HTMS was lower than system with HTMS which were 1.80x1010 GPa and 2.39x1010 GPa respectively. SNP modified interact better with AOS than SNP without HTMS. The interaction between SNP and AOS are important and influence the interface between air and water. Good interaction that were produced able to losse the arrangement at the interface of air and water. Thus, lead to the higher rate of surface tension by time. The addition of HTMS also good in reducing the surface tension of the system. Thus, lead to the good diffusivity of AOS in the system. The higher the maximum rate of surface tension reduction, gave the higher the diffusivity and foaming properties in term of foamability and foam stability [35].

IV. Conclusion

As for the conclusion, the diffusivity of AOS in system that using modified SNP was 0.3099 Å^2/ps while for system using SNP without HTMS was 0.2891 Å^2/ps. The result for surface tension was clearly observed that system using modified SNP lower surface tension that system using SNP without HTMS which was $1.80x10^{10}$ GPa and $2.39x10^{10}$ GPa, respectively after 100 ps. Based on the result, the higher the addition of HTMS will affect the interaction between AOS and SNP. This result related to the statement SNP being modified to become slightly hydrophobic. However, based on the result collected, the surface tension decrease as the foam stability increased. Therefore, the addition of HTMS was good in increasing the stability of foam created.

In order to obtain better result in future work, the characteristic of the atoms involved during construction of molecule, need to be checked carefully. The shape of molecule and the charges of atom involved effect the interaction that was simulated. For dynamic simulation run, the system must be in stable condition in term of energy, density and so on. This is because the data obtained can be affected. However, this can be overcome by running a short dynamics simulation with more than 10 ps simulation time.

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