MOLECULAR-LEVEL COMPUTATIONAL INVESTIGATION OF HYDROCARBON CAPTURE BY SURFACTANT MICELLES

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ABSTRACT:
The amphiphilic surfactant molecules possess unique ability to convert them into diverse shaped and sized micellar structures in the aqueous media. The micellar structures possess a wide range of potential applications particularly in the medical and environmental areas due to the ability of encapsulating nonpolar guest molecules within their hydrophobic internal core. Here, we have analyzed the ability of spherical sodium dodecyl sulfate surfactant micelle to capture a range of hydrocarbons using the computational molecular simulations. We observed that the surfactant micelles, which were initially kept empty, favorably encapsulated the simple hydrocarbons such as methane and hexane from aqueous solution due to the hydrophobic driving forces. Our results demonstrate that surfactant micelles have huge potential in applications such as oil spill treatment due to their distinctive ability of hydrocarbon entrapment.
KEYWORDS: surfactant micelles, hydrocarbon capture, oil spill treatment

INTRODUCTION:
Surfactants are useful in a large number of exceptional applications worldwide owing to their amphiphilic nature [1-3]. According to the surfactants amphiphile nature, they possess double affinity by consisting both "hydrophobic" and "hydrophilic" groups. In general, the hydrocarbon tails of the surfactant molecules are hydrophobic (non-polar) and the heads are hydrophilic (polar) in nature. The polar group possesses functional groups like alcohols, acids, esters, sulphonates, amines, and many more. The hydrophobic part normally possesses alkyl hydrocarbon chains. Surfactants have an excellent ability to alter the surface and interfacial properties at the molecular level [4]. In surfactants chemistry, the term interface has a great importance. The boundary formed or produced between two different phases of matter is called as interface. According to the states of matter, the different kind of interfaces such as gas-solid, gas-liquid or solid-liquid interfaces can exist [26]. When surfactants get adsorbed at the interface, there is significant reduction in surface tension. The addition of little amount of surfactant change the interfacial free energy of the system [27]. The classification of surfactant makes it easier to understand the properties of that particular class and accordingly it is convenient to find their applications. Surfactants possess several types based on the nature of head groups. The four traditional types of surfactants are anionic, cationic, zwitterionic and non-ionic and some new kinds of surfactants with enhanced properties are polymeric surfactants and gemini surfactants [25].

Other than the interfacial property, the second most important property of surfactant molecules is known as self-assembly, which allows the formation of stable micellar structures [27]. This distinctive ability leads the surfactants to be used in many significant areas such as petroleum recovery and processing, pharmaceuticals, personal care products, cleaning agents, surface coatings, crop protection, etc. [1, 3, 4]. Significant number of experimental studies has demonstrated the application of micelles in the various sectors. Nowadays, high speed computer simulation techniques are also used to understand the surface activity of surfactants. Economically the utilization of computational techniques in predicting the physical and chemical properties of the materials is quite affordable and time-efficient.

The individual surfactant molecules play a significant role in several applications, although they can be used in certain crucial applications only by grouping them into 'micelles' (Figure 1) [3, 5]. Such agglomeration of individual surfactants into micellar structure is known as molecular self-assembly [2, 6, 7]. Such assembly of disorganized surfactant molecules into an ordered micellar structure is called as self-assembly, because it occurs due to the local non-covalent interactions between the surfactants in aqueous solution without the help of any external force [7]. Such assembly forms only when the concentration of surfactant molecules in water is reached to a appropriate level, which is called as a critical micelle concentration (CMC) [2, 8]. When CMC is attained, the hydrophobic tails of the surfactants reduce their contact with the aqueous part and aggregate together, which creates a hydrophobic core inside. This leaves the hydrophilic heads to occupy the surface positions of micelle, which remains in continuous touch with water [9].
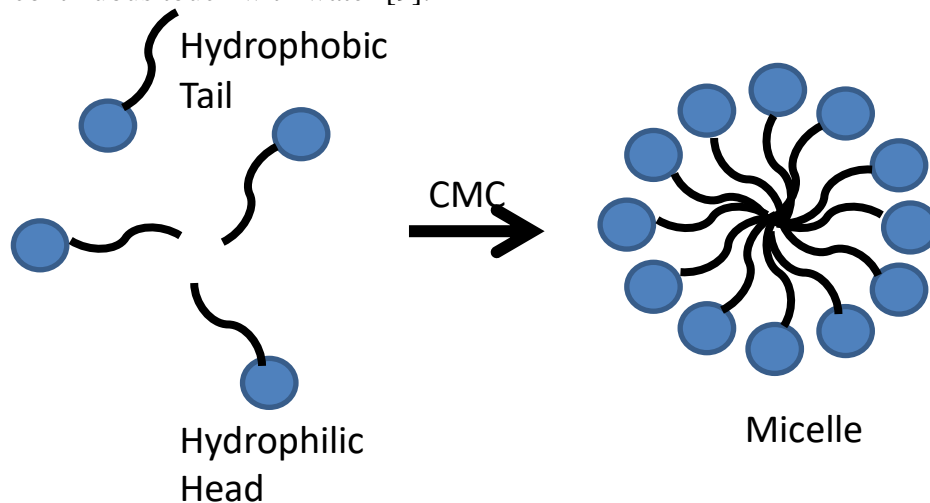

Figure 1. Formation of a spherical micelle structure in aqueous solution at critical micelle concentration (CMC) from individual surfactants molecules, whose hydrophobic tails are shown as black colored lines and hydrophilic heads are shown as blue colored circles.

When organic solvent such as benzene is used instead of an aqueous solution, the surfactants molecules arrange themselves in a reverse manner. The hydrophilic heads occupy the interior position of the micelle and the hydrophobic tails form the exterior layer of the micelle that makes attractive contacts with the organic solvent. Such three-dimensional assembly formation in a reversible manner is known as 'reverse micelle' (Figure 2) [10, 11].
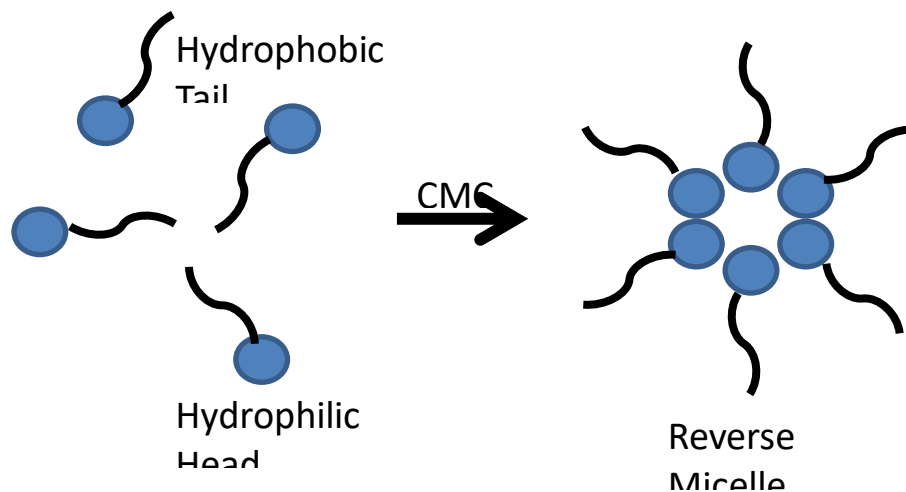

Figure 2. Formation of a spherical reverse micelle structure in organic solution at CMC from individual surfactants molecules, whose hydrophobic tails are shown as black colored lines and hydrophilic heads are shown as blue colored circles.

The maintenance of a stable structure is one of the most important factors in micelle formation. The thermodynamic as well as kinetic stabilities are important for a proper micelle formation. The thermodynamic stability is the factor which is responsible for the process of micelle formation and to reach the equilibrium between the micelles [28]. When the micelle forms, the entropy of the system gets elevated. [29]. The kinetic stability deals with the system changes with respect to time and information of micelle disassemble [29]. It is important for micelle to stay intact before reaching the targeted area. The various factors that influence the stability of micelles are CMC, hydrophobicity to hydrophilicity proportion in surfactant, the interaction between the surfactant chains, temperature and pressure variation as well as the interaction between the micelles and the species that needs to be encapsulated. Various kinds of molecular-level interactions that occur between the surfactant polymers are electrostatic interactions, van der Waals forces and hydrophobic interactions. To form the micelles and to maintain the stability of micellar structure during their application in processes such as hydrocarbon capture, the aforementioned interactions play a significant role. The strength of these interactions decides the fate of formation of micelles or the occurrence of free surfactant polymer chains.

Micelle is a versatile nanostructure that can be also utilized in potential applications like hydrocarbon separation from the aqueous solution, which can have tremendous importance in real-world problems like oil spillage [15]. The oil spillage is a type of water pollution that gets resulted mainly due to ocean related accidents at refining sites or ships, which harms the aquatic animals and plants. The oil gets released into the environment especially on top of water which spoil the aquatic life. The oil layer formed on the surface of water banned oxygen transportation and sunlight to plants and aquatic animals which creates barrier on the way of process of photosynthesis and oxygen deliverance from plants to water. There are number of ways to solve the problem of oil spill such as combustion of spread oil, extraction of spilled oil from water, decomposing the oil film into tiny droplets, etc. All of the above solutions have some advantages and disadvantages. Here, we investigate the process to mitigate oil spill problem, in which the hydrophobic core of micelle can easily encapsulate hydrocarbons such as alkanes due to the attractive interactions between them, which can act as an important process for the success of oil spill remediation.

A significant number of experimental studies have been carried out to understand the micellar structure and micellar interactions with the hydrophobic species such as drugs [12, 13, 14, 16, 17]. However, computational tools like molecular dynamics simulations help to evaluate the time-dependent behavior of any molecular system, which provides a great opportunity to analyze the dynamic features of the solvated micelle [18, 19]. They are also capable of probing a great detail about the features that occurs at the molecular level, which is extremely difficult to investigate using the currently available experimental techniques [2, 3, 5, 11, 20]. In this paper, we perform molecular dynamics simulations of sodium dodecyl surfactant micelles and simple hydrocarbon chains in water for understanding the potential use of surfactant micelle in hydrocarbon separation and the consequent oil spill remediation.

COMPUTATIONAL PROCEDURE:

The molecular dynamics simulations are performed using GROMACS (GROningen Machine for Chemical Simulations) computer simulation package. GROMACS is a versatile simulation tool that can investigate a wide range of molecular systems in detail [22]. In MD simulations, the initial systems are built using AmberTools suite [23]. Using the antechamber module in AmberTools, generalized amber force field parameters and partial charges are applied to surfactants and hydrocarbon molecules [24]. TIP3P water model is used for carrying out the simulations using the explicit water molecules. All the required molecules were combined together using the Packmol package [21]. Also, the systems involving pre-arranged micelle are formed using the Packmol.

Initially, all the systems had undergone energy minimization and equilibration and finally the NPT production runs for a nanosecond time period were carried out. The simulations are carried out at 300K temperature and 1 bar pressure. Anderson thermostat and Berendsen barostat were used to maintain the

temperature and pressure respectively. Other important parameters such as the non-covalent cut-off distance values are implemented properly.

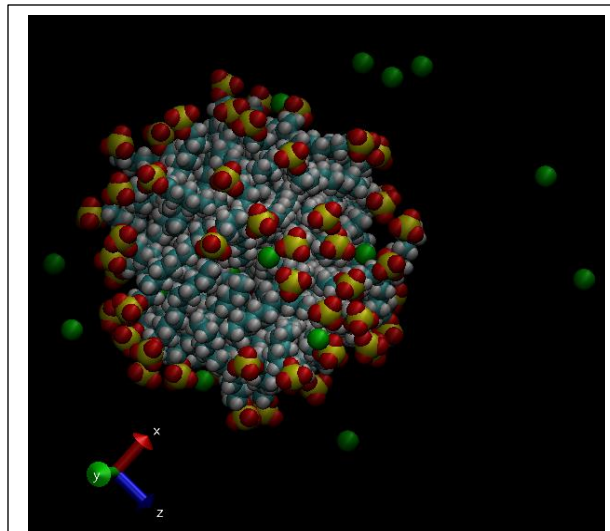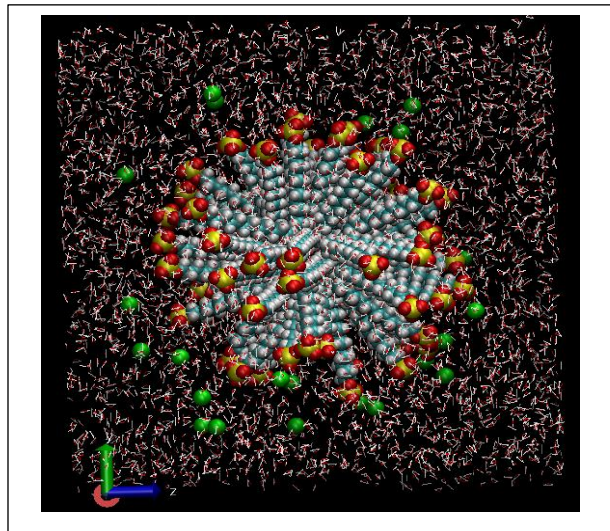## RESULTS AND DISCUSSION:

Figure 3(a). Initial step of MD simulation   Figure 3(b). Final step of MD simulation

This work is especially carried out to investigate the loading capacity of surfactant micelles by using the computationally-intensive molecular dynamics simulation technique. In this work, initially we built a sodium dodecyl sulfate micelle with the help of packmol software, which consists of 60 surfactant molecules. To analyze the loading capacity of micelle, we utilized simple hydrocarbons such as methane and hexane. The simulation system consisted of a sodium dodecyl sulfate micelle and 25 methane molecules solvated in 5000 water molecules. The hydrocarbon tails of surfactants are indicated by blue/white color and the hydrophilic heads are indicated by red/yellow color. The water molecules are indicated by small red/white lines and the methane molecules are indicated by united atom representation and are indicated by green colored spheres (Figure 3(a)). To check the loading capacity of surfactants micelle, we have added the methane molecules to the system and ran the simulation for the period of 1 nanosecond (ns). After 1 ns time period, we got very surprising results; for clarity in vision we hid the water molecules in figure 3(b). We can clearly see that out of 25 methane molecules, 17 methane molecules got entrapped inside the sodium dodecyl sulfate micelle due to the hydrophobic effect. It can be concluded that as the methane molecules are non-polar and water molecules are polar in nature, the methane molecules hide themselves away from water and get captured inside the hydrophobic interior of the micelle. We can still observe the remaining 8 methane molecules staying out of the micelle in figure 3(b). If we will increase the running time of simulation, possibly more methane molecules will get entrapped inside the micelle.

With the same system of surfactants micelle, we further tried to entrap bigger sized hexane molecules inside the micelle. The same system of 60 sodium dodecyl sulfate surfactants micelle and 5000 water molecules, we added 10 hexane molecules inside the simulation box. The simulation ran for 1 nanosecond as shown in figure 4(a). In figure 4(a) the hexane molecules are indicated by green colored chains of hydrocarbons. To see the results clearly, we hid the water molecules in figure 4(b) and observed that 5 hexane molecules got entrapped into the interior of sodium dodecyl surfactant micelle in a very short period of time. This indicates that not only smaller guests like methane, but also bigger hydrophobic guests like hexane can be very well captured inside the surfactant micelle.
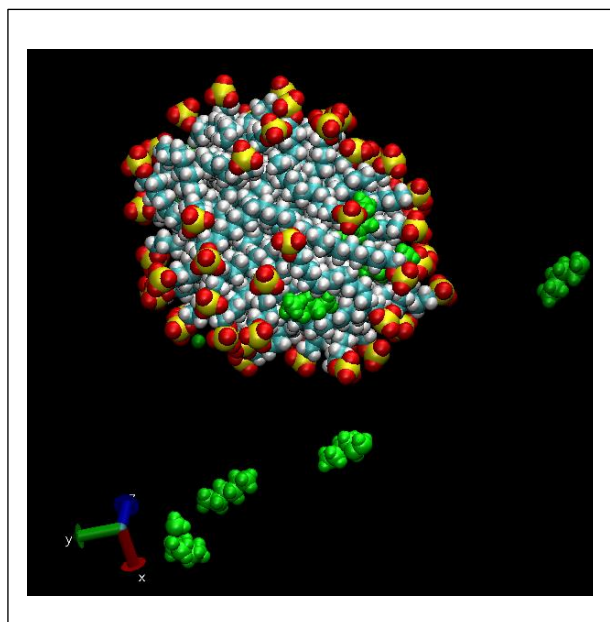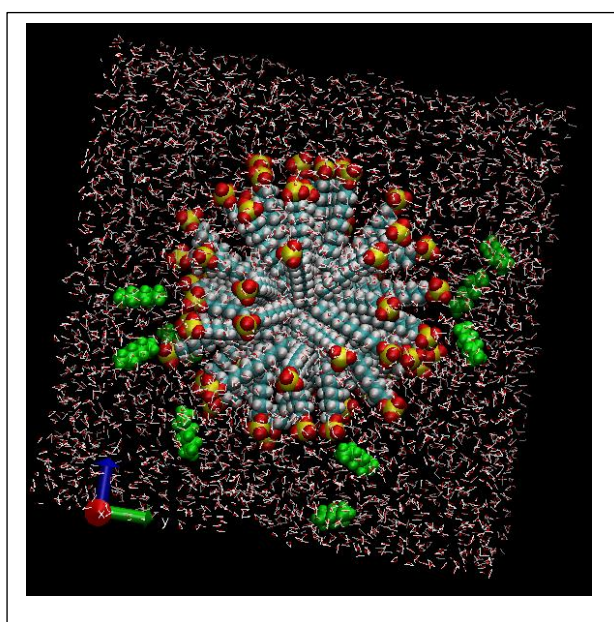
Figure 4(a). Initial step of MD simulation

Figure 4(b). Final step of MD simulation

CONCLUSIONS:

In this work, we have investigated the hydrocarbon loading capacity of the sodium dodecyl sulfate micelle using computational molecular dynamics simulations. In around 1 nanosecond simulation time period, the micelle has entrapped 17 out of 25 methane molecules solvated in 5000 water molecules. Here, the methane molecules due to their hydrophobic nature, tried to hide themselves from water. As the micelles core is also hydrophobic, methane molecules got favorably captured inside the core of the micelle. The comparatively bigger size alkanes such as hexanes were also found to get favorably captured with the same system inside the sodium dodecyl sulfate micelle. All of our results demonstrate that the surfactant micelles are highly capable of entrapping extremely smaller as well as bigger sized hydrophobic molecules inside and can have wide applications in petroleum industry such as hydrocarbon separation and oil spill treatment.

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