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Molecular Dynamics Simulation of Aggregates in Dodecane/Span80 System

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Abstract -Molecular dynamics simulation of self-assembly of surfactant span80 molecules to form reverse micelle in nonpolar liquid dodecane was carried out. Simulations were performed using united atom model for dodecane and hybrid model for span80 molecules. Simulations were carried out for various concentrations of surfactant molecules and water. Formation of aggregates at various stages of simulation was analysed. Physical dimension of the reverse micelle formed in the simulation were measured and its diffusion coefficient was calculated. Various characteristics of reverse micelle such as aggregation number, diameter and radius of water core were compared with available experimental results.

Keywords: Molecular dynamics simulation, dielectric liquid, surfactant, reverse micelle, size and diffusion coefficient.

1. Introduction

Electrohydrodynamic flow (EHD) in dielectric liquid is a multi-physics problem involving fluid mechanics, electrochemistry and electrostatics. Number of ions in dielectric liquid is negligible, but the presence of impurities could be a source of free ions, when the dielectric liquid is subjected to electric field. Free cations and anions generated due to ion dissociation can combine again in recombination process to form neutral ion pairs (Suh and Back, 2013). Addition of surfactant molecules increases the free ion concentration as some of the free ions get solvated in the reverse micelle formed by the self-assembly of surfactant molecules around the water molecules in the dielectric liquid, which prevents the recombination of ions (Dukhin and Goetz, 2006). In reverse micelle, hydrophilic head portion of surfactant molecules gets attached to the water core (which is formed by the aggregation of water molecules in the dielectric liquid) and the hydrophobic tail portion gets aligned away from the water core. Diffusion of reverse micelle also exerts major effect on the ion transport in the dielectric liquid, which is thus critical in the EHD phenomenon in the same.

Reverse micelle is formed in dodecane/span80 mixture, as previously reported by an experimental study (Abou-Nemeh and Bart, 1998). Molecular dynamics simulation of formation of reverse micelle in dodecane/span80 mixture has not been reported so far, to the best of our knowledge. Objective of our study is to perform molecular dynamics simulation of dodecane/span80 system, in order to verify the formation of reverse micelles in the same. Various stages of formation of aggregates in the above system need to be analysed and the dimension of the aggregates needs to be measured for calculating the diffusion coefficient of reverse micelles.

2. Method

Dodecane was modelled using united atom model, in which 12 united carbon atoms describes the molecule. To model the span80 (Sorbitan Monooleate) molecule, we used a hybrid model, reported in the literature (Han, 2012), which has the hydrophobic tail represented by 17 united carbon atoms and the

hydrophilic head represented by an all atom model. TIP3P model was used for water. CHARMM force field parameters were used for simulations and the parameters for span80 were taken from previously reported work (Nunez-Rojas and Dominguez, 2013). Simulation boxes corresponding to various concentrations of span 80 and water in dodecane were constructed using Packmol package and all simulations were performed by using the NAMD software.

Simulations were conducted on periodic boundary conditions and long range electrostatics interactions were calculated with Particle Mesh Ewald method. Energy minimization was done for 0.1 ns and all production runs were done using NVT ensemble, with times step of 2fs. Each simulation was done for a time period of 80 ns and total energy of the system was monitored to determine the equilibrium state of the system. To calculate properties of the aggregates formed in the system, data from the last 4 ns were sampled. Visualization and various analyses were done using VMD package.

Diffusion coefficient was calculated from the mean-square-displacement (MSD) vs time plot. To validate the model, diffusion coefficient was calculated for span80 in dodecane and the value obtained from MD simulation was compared with the value obtained using Einstein-Stokes equation, in which hydrodynamic radius of span 80 molecule calculated by accessible surface area method was used.

3. Result

Formation of aggregates in the dodecane/span80 system was observed in the MD simulation. To verify the formation of reverse micelle, two kinds of radial distribution function (RDF) were plotted; the first one is between water core and the tail of span80 molecule and the other is between water core and the head of span80 molecule. It was found that the first peak in the plot of RDF between the water core and the head group is nearer to the water core compared to the first peak in RDF between the water core and the tail group, which confirms the formation of reverse micelle. Radius of water core was measured and averaged over the values in 3 axes and the radius of and the radius of reverse micelle was taken from the radius corresponding to the peak in RDF between the water core and the tail group. Aggregation number was also counted. These values were found to be consistent with the experimental results (Abou-Nemeh and Bart, 1998). Subsequently, diffusion coefficient of reverse micelle was also calculated.

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