Research Paper

Pathway and energetics of the thermally-induced structural changes in microemulsions

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HIGHLIGHTS

- Thermal decomposition of microemulsions is studied using molecular simulations.
- The evolution of microemulsion's structure during decomposition is clarified.
- The energetics of microemulsion's thermal decomposition is elucidated.

ARTICLE INFO

ABSTRACT

Microemulsions are thermodynamically stable dispersions of nano-droplets stabilized by surfactants. In water-in-oil microemulsions, the nano-droplets exist in the form of swollen reverse micelles. Recent experiments demonstrated very high critical heat fluxes (CHF) in boiling of water-in-oil microemulsions, which makes these microemulsions ideal heat transfer fluids for high heat-flux thermal management applications. While the nanoscale structure of the microemulsions is inevitably changed during their boiling, little is known about such change and its energetics, which are critical for understanding the microemulsion boiling. Here we report a study of the pathway and energetics of thermally-induced structural change in water-in-oil microemulsions using microsecond-long molecular dynamics simulations. We show that, for microemulsions that are thermodynamically stable at room temperature, upon increasing their temperature to similar to that found in boiling experiments, their spherical reverse micelles transition to cylindrical wormlike reverse micelles through merging and splitting of individual reverse micelles. These structural transitions are accompanied by a gradual release of water molecules from the reverse micelles. These transitions are endothermic with the heat absorption dominated by the release of water molecules from the water core of the reverse micelles. The release rate of water molecules from the interior of reverse micelles, hence the heat absorption rate, slows down as the structural transition proceeds because the remaining water molecules in the interior bind more strongly to the polar moieties of the surfactants.

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1. Introduction

Stable mixture of polar and apolar liquids is difficult to achieve due to the segregation tendency of these liquids. However, when suitable type and amount of surfactants are introduced, thermodynamically stable dispersions of polar liquids in apolar liquids (or vice versa) can be obtained and these dispersions are termed microemulsions. Two common types of microemulsions are water-in-oil microemulsions and oil-in-water microemulsions [1]. Here "*water*" refers to a polar phase and "*oil*" refers to an apolar organic phase. The dispersed phase often exists as nanostructured entities stabilized by surfactant molecules. These entities, with characteristic dimensions as small as a few angstroms are termed swollen reverse micelles (RM) in water-in-oil microemulsions or swollen micelles in oil-in-water microemulsions [1]. Because of their unique properties such as the nanoscale size of their internal structures, microemulsions have a wide range of applications including drug delivery, chemical synthesis, and enhanced oil recovery [2–4].

While microemulsions have been used extensively in industrial applications since their discovery, they have rarely been used in heat transfer applications until recently [5–8]. In particular, one

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of us has developed water-in-polyalphaolefin (PAO) microemulsions as heat transfer fluids for high heat-flux cooling [5–7]. At low water loading and room temperature, this microemulsion features spherical RMs, whose radii vary from 1.3 to 9.6 nm when the water concentration in the microemulsion increases from 1.8 to 4.5%. The viscosity and thermal conductivity of this microemulsion are only slightly higher (<20%) than those of the pure PAO liquids. Using this microemulsion as heat transfer fluids, nucleate boiling was observed in the pool boiling experiments and critical heat flux (CHF) as high as 500 W/cm^2 was achieved without modifying the microstructure of the heater surfaces [7]. The water vapor released during boiling, once condensed, self-assembled spontaneously with the surfactant molecules in the liquids to form RMs, which makes microemulsion suitable for closed-loop operations in thermal management system. These results suggest that microemulsions may offer a new method for achieving superior CHF in practical engineering applications. This method is potentially more robust compared to the classical method of introducing microstructures to the heater surfaces. This is because, the microstructure of heater surfaces is often inevitably modified during operation (e.g., by fouling), which compromises the CHF in long-term operations and/or in aggressive working environments. For example, it is known that the enhancement of CHF observed for nanofluids is highly variable and often deteriorates over time [9].

The fundamental understanding of the boiling of microemulsions is limited at present. This, along with the fact that numerous microemulsions can be engineered by tuning the type and loading of the polar/apolar fluids and the surfactant molecules, makes it difficult to optimize microemulsions for achieving better boiling performance. To gain insight into the boiling of microemulsions, it is essential to clarify the formation, growth, and departure of bubbles, and how these bubble dynamics are coupled with the fluid flow and heat transfer during boiling. While these problems have been clarified to a large extent for boiling of pure liquids in prior research, applying the insight from those prior studies to the boiling of microemulsions is not straightforward due to the emergence of new issues. Some of the most important new issues are how the structure of the RMs changes in response to elevated temperature, how polar molecules are released during boiling of microemulsions, and how heat is absorbed during this process. These issues are unique to the boiling of microemulsion, and clarifying them is a necessary step toward understanding the microemulsion boiling.

While the phenomena of polar molecules being released from RMs during boiling of microemulsions and the associated heat absorption are evident in experiments (e.g., formation of visible bubbles and effective heat removal from heater surfaces), little is known about the nature of these processes. Conceivably, the internal nanostructures of the microemulsions are changed during boiling, but it is not clear what pathways the structure change follows and how they affect the water release and heat absorption. Such a limited understanding, despite decades of study of microemulsions, is due to the fact that the phase and structural change of microemulsions under conditions similar to that in boiling of microemulsions was rarely studied in the past. Specifically, prior studies focused on phase change at moderate temperature (typically <60 °C, i.e., much lower than the boiling temperature of water) while temperature higher than 100 °C is often found in boiling of microemulsions [7]. Prior studies of the phase change in microemulsions were mostly performed under quasi-equilibrium conditions (i.e., the temperature was changed very slowly), but the temperature of microemulsions changes greatly over millisecond time scales as they move past the heater surface.

In the present work, we investigate the evolution of the internal nanostructure of microemulsions at high temperature and the associated energy changes. Specifically, we examine how water molecules are released from water-in-oil microemulsions when the temperature of the microemulsion is raised to temperature close to the boiling temperature of bulk water using microsecond-long molecular dynamics (MD) simulations. MD simulations have been used successfully to study self-assembly of micelles [10–23], thermal transport, and phase changes [24,25], and are thus capable of studying the thermally-induced changes of microemulsions. Here, the release of water molecules and the associated heat absorption are quantified, and the molecular details of the structural change of the microemulsions during water release are provided. The rest of the paper is organized as follows. Section 2 presents the molecular models and methods for our MD simulations. Section 3 presents the structural changes and associated energy change of the microemulsions at high temperature. Finally, conclusions are drawn in Section 4.

2. Simulation models and methods

We use MD simulations to study the thermally-induced structural change of water-in-oil microemulsions. Fig. 1 shows a sketch of the simulation system. The system includes two water-swollen RMs stabilized by sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and the oil phase of the microemulsion is taken as n-octane fluids. Each RM consists of 42 AOT molecules and 210 water molecules (note that each AOT molecule contains one Na$^+$ ion). This gives a water-to-surfactant ratio ($W_0 = [H_2O]/[AOT]$) of five, which is common for water-in-oil microemulsions. There are 6000 n-octane inside the system to ensure a high mass fraction of the n-octane liquids. The microemulsion is placed on top of a solid wall to form a film of ~11 nm in thickness at 300 K. The wall is modeled as a square lattice of carbon atoms. The system contains a total of 175,348 atoms. A free space is introduced above the microemulsion film to accommodate the water molecules released from the RMs during the simulations. The simulation box measures 18.8×9.4 nm^2 in the xy-plane and 20 nm in the z-direction. Periodical boundary conditions are applied in all three directions.

All-atom models are adopted for the AOT, water, and n-octane molecules. The SPC/E model is used for the water molecules. The force fields for AOT molecules are the same as those used by Abel et al. [10,26], which were derived from the CHARMM family of force fields [27]. The force fields for the n-octane molecules are derived from the CHARMM36 all-atom parameters for lipids [27].

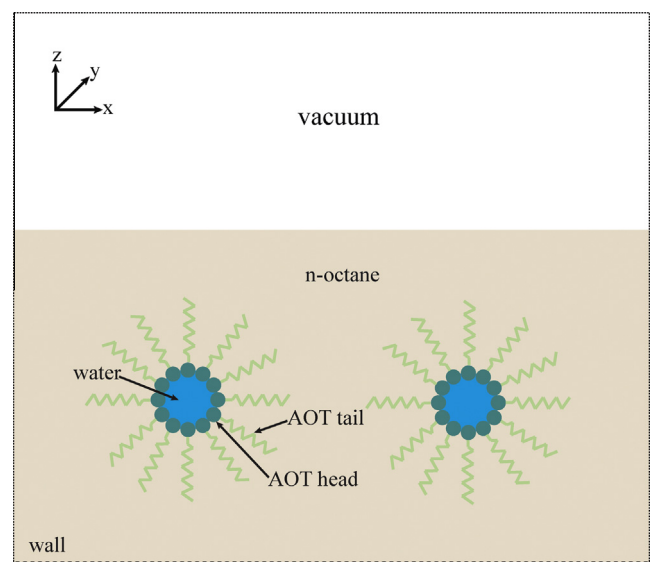**Fig. 1.** A schematic of the simulation system. The black dashed lines indicate the MD simulation box, which is periodical in all three directions.