**PRF** # 57523-DNI9
**Project Title**: **Mesoscale Modeling of Nanoemulsion in Porous Media**
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The goal of this project is to obtain a mechanistic understanding of the formation and stability of nanoemulsion structure in porous media with relevance to enhanced oil recovery (EOR). Nanoemulsion provides a potentially cost-effective alternative to microemulsion EOR, but much of the fundamental knowledge required to assess its feasibility remains absent. The project will develop a mesoscale model to address important issues of this approach including the in-situ production and stability of nanoemulsion within porous media. Support from this project has allowed the continuous development of parallel computer code for emulsion simulations, which has been implemented on high-performance computing clusters such as Stampede2 at the Texas Advanced Computing Center. It also provides valuable training to a graduate student on the soft matter physics, high-performance computing and scientific visualization.

In the current project period, we investigated the autocatalytic behavior of micelles in details. In the simulations, a micelle nucleus will evolve into a cluster which contains hundreds of micelles through repeated fissions as demonstrated in Figure 1a.

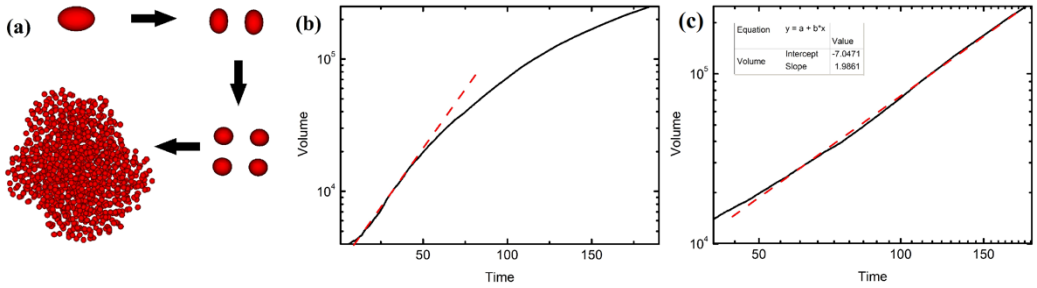


**Figure 1** (a) Snapshots of continuous micelle fissions. Growth curve of micelle total volume as a function of time in (b) log-linear and (c) log-log scales.

A major finding from our study is the existence of two stages in micelle splitting process (Fig. 1b-c). The micelle volume $V_{\text{tot}}$ exhibits an exponential growth at the first stage, which indicates that all of the micelles actively split during this period. At the second stage, the growth rate reduces to a power law growth behavior, $V_{tot} \propto t^2$. The slow-down results from the depletion of surfactant monomers within the micelle cluster, which reduces the monomer supersaturation and causes micelles inside the cluster to stop splitting. Fig. 2a shows that the monomer depletion is limited by the diffusion of monomers from the surrounding solution into the micelle cluster.

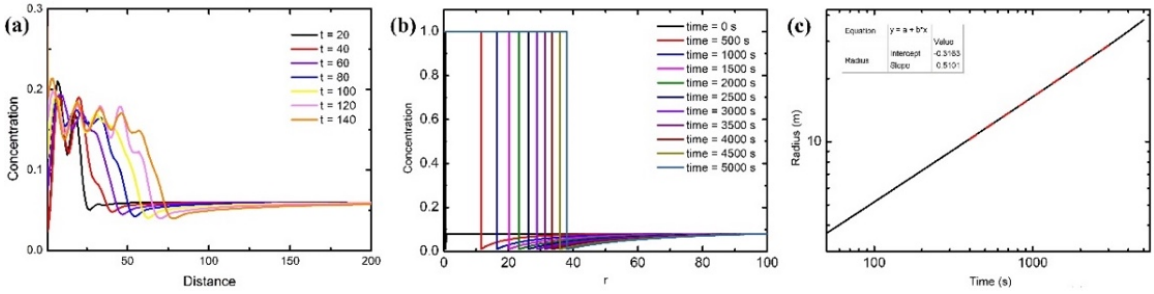


**Figure 2** (a) Radial distribution of surfactant concentration (both in micelles and solution) at different times. (b) Radial distribution of surfactant concentration and (c) cluster radius calculated from the analytical model.

An analytical model is developed to describe the diffusion-limited micelle splitting process. The model treats the growth of micelle cluster in a similar way as a secondary phase particle growing in the matrix. The monomer in-flux at the micelle cluster boundary is given by $D\frac{\partial c}{\partial r} = M(c - c_\alpha^{eq})(c_\beta^{eq} - c)$, and the growth rate of cluster radius is $\frac{dR}{dt} = D\frac{\partial c}{\partial r}/(c - c_\beta^{eq})$, where $c_\beta^{eq}$ / $c_\alpha^{eq}$ are surfactant concentrations inside/outside the cluster boundary and $c_0$ is the far-field concentration. The surfactant concentration distribution obtained from the model (Fig. 2b) is similar to the phase-

field simulation. The model predicts an exponent of 1.5 for total micelle volume (Fig. 2c), which is close to the result from simulation.

We also found that the duration of the first stage with exponential growth behavior is influenced by the competition between the micelle reaction and monomer diffusion kinetics. As shown in Fig. 3, the first stage is shortened when the monomer diffusivity is decreased. This suggests that enhancing monomer transport, e.g. by introducing hydrodynamic flow, is useful to increase the micelle production rate through splitting.

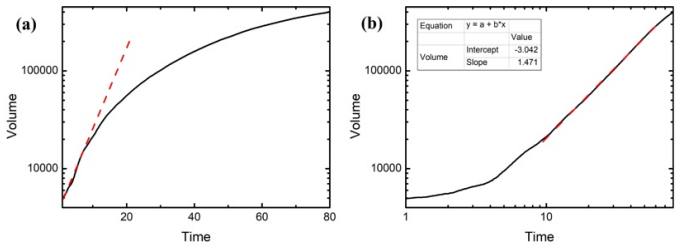


**Figure 3** Growth curve of total micelle volume as a function of time in (b) log-linear and (c) log-log scales.

In the current project period, we further extended the phase-field model to the water-oil-surfactant ternary system. The total free energy of the ternary system is expressed as:

$$F = \int f_\phi(\phi) + f_c(c) + \frac{\nu(c)}{2}(\nabla\phi)^2 + \frac{\nu_c}{2}(\nabla c)^2 + 2\lambda(c)H_0^2(\nabla\phi)^2 - 4\lambda(c)H_0|\nabla\phi|\nabla^2\phi + \frac{\lambda(c)}{2}(\nabla^2\phi)^2$$

Where ϕ and c are the oil phase fraction and surfactant concentration, respectively. Compared to the surfactant-water model, a parabolic function $f_c(c) = \alpha c^2$ is introduced to represent the homogenous free energy of surfactants, and coefficient ν(c) is made a function of surfactant concentration to describe the effect of surfactant adsorption on water/oil interface in reducing the interface energy. Preliminary study shows that the model is able to produce nanoemulsion structure that is consistent with the prediction of the classic curvature-elastic model (Fig. 4).

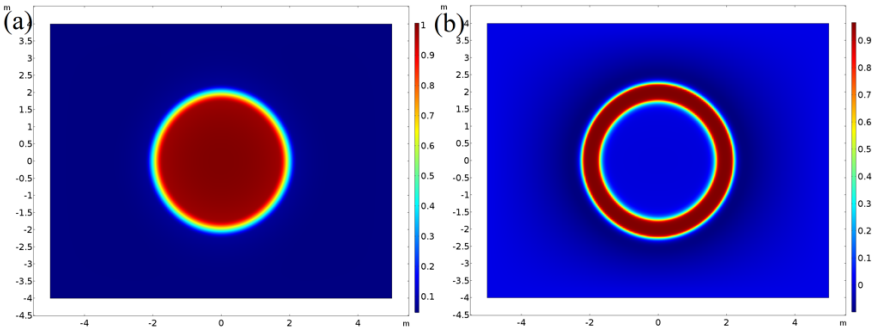


**Figure 4** (a) oil and (b) surfactant concentration distributions of a micelle calculated according to the ternary model.

A numerical procedure is established to evaluate model parameters from the physical properties of the emulsion system. In particular, we derived a simple fitting function based on simulation results to estimate two important parameters α and $\nu_{min}$ from the interface energy and width of the microemulsions (Fig. 5).

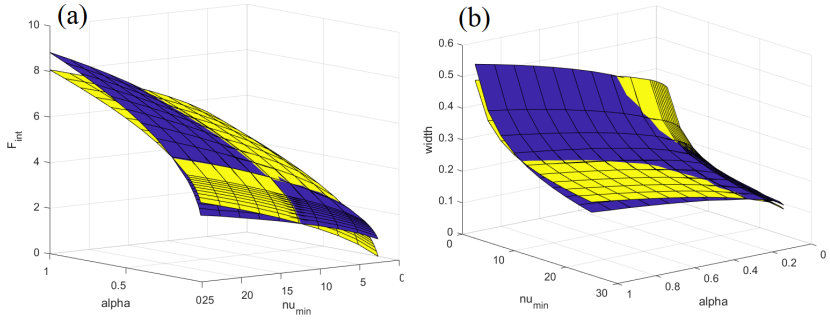


**Figure 5** (a) Interface energy and (b) interface width of a microemulsion as in simulations (blue surface) with different α and $\nu_{min}$ values and fitting results (yellow surface).