Coarse-Grained Model Simulation of Surfactant Solution in Couette Flow: Postprint

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Abstract

This study employs coarse-grained molecular dynamics methods to investigate micelle formation, velocity distribution, and rheological behavior in aqueous surfactant solutions at various concentrations under Couette flow. The results indicate that for surfactant solutions at the same concentration, the time required for micelles to reach complete dynamic equilibrium decreases with increasing shear rate; concurrently, as surfactant molecule concentration increases, the micelle dynamic equilibrium time also decreases, resulting in more rapid micelle formation. Regarding the relationship between shear rate and solution shear viscosity, at a fixed surfactant molecule concentration, the shear viscosity gradually decreases with increasing shear rate, exhibiting shear-thinning characteristics.

Full Text

Preamble

A Coarse-Grain Molecular Dynamics Simulation for Surfactant Aqueous Solution in Couette Flow

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Abstract

This paper investigates micelle formation, velocity distribution, and rheological behavior in surfactant aqueous solutions under Couette flow using coarse-grained molecular dynamics simulations. The results demonstrate that for surfactant solutions at a given concentration, the dynamic equilibration time for micelle formation decreases progressively with increasing shear rate. Conversely, at a constant shear rate, higher surfactant molecular concentrations lead to shorter dynamic equilibration times and faster micelle formation. Regarding the relationship between shear rate and solution viscosity, the simulations reveal that under constant surfactant concentration, shear viscosity decreases with increasing shear rate, exhibiting characteristic shear-thinning behavior.

Keywords: surfactant aqueous solution; coarse-grained molecular dynamics simulation; Couette flow; shear viscosity

Introduction

As global energy demands continue to grow, the development of new energy sources and the efficient utilization of existing resources have become increasingly critical. Drag reduction represents an effective method for decreasing flow resistance in pipelines, thereby achieving significant energy savings. Consequently, research on drag-reducing surfactants has emerged as a prominent area of investigation [1-4]. Since the microstructure of surfactants in solution fundamentally governs their rheological properties, a comprehensive understanding of micelle formation and rheological characteristics is essential.

Current research on surfactant solutions primarily relies on experimental measurements, where macroscopic rheological data are used to infer microstructural properties or direct electron microscopy observations are employed to visualize surfactant aggregates [5-7]. In the realm of microstructural simulation, most molecular dynamics studies have focused on micelle formation, breakup, and rheology of conventional polymers, while investigations specifically addressing amphiphilic surfactants remain limited. Notable contributions include the work of N.A. Volkov and N. Arai. Volkov [8] conducted molecular dynamics simulations of micelle formation in sodium dodecyl sulfate (SDS) solutions, demonstrating that NaCl addition promotes the formation of larger micelles and providing detailed characterization of micelle morphology. Arai [9] employed dissipative particle dynamics (DPD) to investigate the rheological properties of surfactant solutions in nanoscale parallel channels under shear flow, revealing that hydrophobic-hydrophilic chemical modification of nanochannel surfaces can induce a transition from shear-thinning to shear-thickening behavior. Sambasivam [10] pioneered the use of coarse-grained molecular dynamics (CGMD) to simulate the deformation and breakup of rod-like micelles in CTAC+NaSal solutions under shear flow, analyzing monomer micelle lengths and orientation distributions through energy-based methods, and determining an average CTAC micelle length of 5.4 nm over a total simulation time of 3 s. In quantitative studies of micelle formation time and size, Wataru Shinoda [11] simulated the self-assembly of several nonionic surfactants at air-water and oil-water interfaces, providing quantitative calculations of micelle size and formation kinetics. Regarding the rheology of coarse-grained surfactant solutions under high shear rates in Couette flow, J. Castillo-Tejas [12] performed coarse-grained non-equilibrium molecular dynamics simulations of CTAC surfactant solutions in both Couette and Poiseuille flows, introducing a novel coarse-grained representation of CTAC monomers consisting of one hydrophilic head group and four hydrophobic tail groups. This work established quantitative relationships between shear velocity and shear stress, as well as shear velocity and shear viscosity, across different surfactant concentrations. Extending this approach, E.O. Castrejón-González [13] simulated water-surfactant-oil mixtures in Couette flow at high shear rates, observing complex rheological transitions from Newtonian to shear-thinning, then to shear-thickening, and potentially back to Newtonian behavior with increasing shear rate.

Despite these advances, studies of micelle formation time have typically employed detailed atomistic models, which suffer from poor generality and prohibitive computational cost. The present work addresses this limitation by employing coarse-grained molecular dynamics to simplify the treatment of molecular polarity and inter-group forces, enabling efficient determination of micelle formation times. Furthermore, compared to previous investigations, this study systematically examines the effects of both concentration and temperature on surfactant rheology, providing qualitative analysis that yields insights consistent with macroscopic experimental observations.

1 Numerical Methods

The simulation domain for the surfactant solution measured 30 × 20 × 15 in the x, y, and z directions, respectively (with wall regions occupying y-coordinates from 0 to 20). Each coarse-grained surfactant molecule comprised one hydrophilic head group (diameter) and four hydrophobic tail groups (diameter), while coarse-grained water molecules also had diameter . Interactions between surfactant head-head, head-water, tail-tail, and water-water pairs were modeled using the Lennard-Jones (12-6) potential, whereas repulsive interactions between surfactant head-tail pairs and tail-water pairs were described by the LJ 9-6 potential, as illustrated in [Figure 1: see original paper].

[Figure 1: see original paper] Surfactant and water CG molecule interaction schematic

Intramolecular bonds between adjacent head-tail and tail-tail groups within surfactant molecules were governed by harmonic potential models. The surfactant solution employed the NVT ensemble, while solid walls utilized the NVE ensemble. The coarse-grained surfactant solution in Couette flow is depicted in [Figure 2: see original paper].

[Figure 2: see original paper] The surfactant aqueous solution in Couette flow schematic

1.1 L-J Model

The L-J (12-6) potential is expressed as:

$$U_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

with a cutoff radius of 2.5 .

The repulsive potential function can be approximated by the LJ 9-6 model:

$$U_{rep}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{9} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

1.2 Harmonic Model

The harmonic potential function is expressed as:

$$U_{harm}(r) = \frac{1}{2}k(r - r_0)^2$$

where the force constant k = 5.0 and equilibrium distance r = . Cross-interaction parameters were determined through the Lorentz-Berthelot combining rules.

1.3 NVT and NVE Ensembles

The NVT canonical ensemble (employing Nose-Hoover thermostat) is governed by:

$$\dot{\mathbf{r}}_i = \mathbf{v}_i$$

$$\dot{\mathbf{v}}_i = \frac{\mathbf{F}_i}{m_i} - \xi\mathbf{v}_i$$

$$\dot{\xi} = \frac{1}{Q}\left(\sum_{i=1}^{N} m_i v_i^2 - Lk_BT\right)$$

where $\mathbf{r}_i$, $\mathbf{v}_i$, and $\mathbf{F}_i$ represent the position, velocity, and force on particle i; T is the target temperature; L is the number of degrees of freedom; is the thermodynamic friction coefficient; Q is the thermostat mass defined as $Q = \tau^2 Lk_BT$, with being the system relaxation time.

The NVE ensemble, applied primarily at the walls, conserves the number of atoms, total energy, and system volume.

1.4 Additional Simulation Details

Initial configurations of coarse-grained molecules were generated using Material Studio, with the resulting coordinate data serving as initial conditions for the simulations. In these non-equilibrium molecular dynamics (NEMD) simulations, the dimensionless time step was 0.001 for all cases, with each simulation run for 1.5 million steps (approximately 5.5 ns).

**** Dimensionless formulas for physical parameters

Physical Quantity	Dimensionless Formula
Density	$\rho^* = \rho\sigma^3/m$
Shear Rate	$\dot{\gamma}^* = \dot{\gamma}\sqrt{m\sigma^2/\epsilon}$
Force	$f^* = f\sigma/\epsilon$
Pressure	$p^* = p\sigma^3/\epsilon$

3 Results and Discussion

3.1 Micelle Formation Time Analysis

Through visualization of micelle formation processes using the open-source software OVITO (Open Visualization Tool), the time required for coarse-grained surfactant molecules to form micelles was determined for six shear rate conditions: 0.03, 0.06, 0.1, 0.15, 0.2, and 0.25. The typical micelle formation process generally follows four stages: initial state → small micelle clusters → large micelle clusters → complete dynamic equilibrium. This evolution is illustrated for a surfactant concentration of 0.20 and shear rate of 0.1 in [Figure 3: see original paper].

[Figure 3: see original paper] The dynamic equilibrium state of micelles: (a) initial state at 0 ns, (b) small micelle clusters at 0.37 ns, (c) large micelle clusters at 0.73 ns, (d) complete dynamic equilibrium at 3.28 ns

The relationship between shear rate and micelle formation time for surfactant concentrations of 0.05, 0.15, and 0.20 is presented in [Figure 4: see original paper]. The data reveal that for each concentration, the dynamic equilibration time decreases monotonically with increasing shear rate of the Couette flow upper plate (shear rates: 0.03, 0.06, 0.1, 0.15, 0.2, 0.25). Furthermore, at any given shear rate, higher surfactant concentrations yield shorter dynamic equilibration times, indicating accelerated micelle formation.

[Figure 4: see original paper] Shear velocity and micelle formation time

3.2 Surfactant Concentration and Velocity Distribution

To investigate the influence of surfactant micelles on the Couette flow field, velocity distributions were examined at a shear rate of 0.1 for micelle concentrations of 0, 0.05, 0.15, and 0.20, as shown in [Figure 5: see original paper]. The velocity profiles were obtained by dividing the y-direction (velocity gradient direction) into 100 equally spaced slabs from y = 0 to y = 20, each with volume 30 × 0.2 × 15 . Time-averaged velocities of coarse-grained particles (including surfactant molecules and water) within each slab were computed after the system reached dynamic equilibrium.

[Figure 5: see original paper] The relationship between micelle concentration and spatial mean velocity distribution

The results indicate that for pure water (surfactant concentration = 0, black line), the velocity distribution is essentially linear with a slope of 1. Upon addition of surfactant molecules, the average velocity in the region y = 0–11 exceeds that of pure water, while velocities in the region y = 11–20 fall below pure water values. However, the data do not support a simple correlation between surfactant concentration and the magnitude of velocity profile deviation. For instance, at y = 11–20 , the concentration 0.15 case shows greater deviation from the pure water profile than the concentration 0.20 case. Consequently, no definitive relationship exists between surfactant concentration and the degree of modification to the Couette flow velocity distribution.

3.3 Relationship Between Shear Rate and Shear Viscosity

Shear viscosity was calculated from shear stress and shear rate according to:

$$\eta = \frac{\tau}{\dot{\gamma}}$$

where is shear viscosity, is shear stress, and $\dot{\gamma}$ is shear rate. All calculations employed dimensionless quantities.

The relationships between shear rate and shear stress, and between shear rate and shear viscosity, are presented in [Figure 6: see original paper] and [Figure 7: see original paper] for dimensionless temperature T = 1.35 and shear rates of 0.01, 0.025, 0.05, 0.1, 0.15, 0.2, and 0.25.

[Figure 6: see original paper] The relationship between shear rate and shear stress
[Figure 7: see original paper] The relationship between shear rate and shear viscosity

[Figure 6: see original paper] demonstrates that shear stress increases with shear rate, and higher coarse-grained surfactant concentrations produce greater shear stress. [Figure 7: see original paper] reveals that at low shear rates (0.01 and 0.025), the viscosity data appear scattered and do not exhibit clear shear-thinning characteristics. However, for shear rates above 0.03, viscosity decreases systematically with increasing shear rate, demonstrating pronounced shear-thinning behavior. At very low shear rates (<0.03), thermal motion of coarse-grained molecules introduces significant noise, preventing the formation of orderly Couette flow across fluid layers. Therefore, analysis was restricted to the effective shear rate range of 0.05–0.25. Additionally, a positive correlation exists between surfactant concentration and shear viscosity: higher surfactant concentrations yield greater shear viscosity.

Conclusion

This study conducted non-equilibrium molecular dynamics simulations of surfactant solutions in Couette flow across various concentrations, elucidating the relationships between shear rate and micelle formation time, surfactant concentration and velocity distribution, and shear rate with both shear stress and shear viscosity. The findings indicate that both surfactant concentration and shear rate are negatively correlated with micelle formation time, while no definitive correlation exists between surfactant concentration and modifications to the velocity profile. At fixed concentration, increasing shear rate produces higher shear stress but lower shear viscosity, characteristic of shear-thinning fluids. These parametric analyses provide deeper insights into micelle formation mechanisms and rheological properties of surfactant solutions, establishing a foundation for understanding drag reduction phenomena.

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