Dynamics and Rheology of Micellar Fluids from Molecular Dynamics Simulations

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Summary Coarse grained Molecular Dynamics (MD) simulations with explicit solvent- and salt-mediated interactions are developed to study the dynamics of cationic cylindrical micelles in shear flow. Single micelle simulations are used to study the effect of shear rate on flow alignment-tumbling cycles, micelle elongation and rupture. Binary interactions and flow-induced micelle coalescence are also studied under different salt concentrations to understand the molecular origin of the shear-thickening behavior seen in micelle solutions.

It is well-known that thermodynamic self-assembly of amphiphilic molecules results in micellar structures of different shapes such as spheres, rods, vesicles, or lamellae. In the case of ionic surfactants, the phase behavior is dictated by surfactant concentration, temperature as well as concentration and chemical structure of counterions or added salt. The equlibrium phase behavior of surfactants is greatly influenced by flow deformation. For instance, both shear thinning and shear thickening behaviors are observed in cylindrical or wormlike micelle solutions depending on the salt to surfactant ratio: see [1] and references therein. Shear thinning response is attributed to flow-alignment and/or breakage of wormlike micelle networks. Shear thickening is hypothesized to be the manifestation of a kinetic aggregation process in which flow-aligned micelles coalesce to form longer structures which eventually form an entangled network [2, 3]. Recently, it has been observed that dilute cationic rodlike micelle solutions containing organic salts such as sodium salicylate, when subjected rapidly to a sufficiently large flow deformation rate comparable or greater than the inverse of the micelle rotational diffusion time scale, can form irreversible gel-like phases[4]. Overall, it appears that such intriguing non-equilibrium phase transitions require the satisfaction of both *chemical* and *mechanical* criteria, the chemical one being the saturation of the micelle corona with hydrophobic counter-ions leading to efficient electrostatic screening[5,6] and the mechanical one being that a Peclet number, defined as the ratio of the micelle diffusion time scale to the inverse shear rate, should exceed an O(1) value to cause appreciable flow-alignment of the micelles[1-4].

The abovementioned interplay between specific chemical interactions and flow-induced configurational changes suggests that gaining a comprehensive mechanistic understanding of the dynamics and rheology of micelle solutions requires a theoretical framework that accounts explicitly for solvent polarizability and electrostatic forces. Molecular investigations of phase transitions in self-assembled structures of surfactants, e.g. sphere to rod transition in micelles, are limited by the length and time scales that can be sampled by popular simulation methods such as molecular dynamics (MD). Multiscale simulations using coarse-grained (CG) representations of surfactants or micelles, which can sample dynamics over several microseconds, are often employed to overcome the limitations of atomistic MD. We have developed an efficient multiscale modeling scheme to study phase transitions, as well as, binary interactions of self-assembled micelles of cationic surfactants[5, 6]. Our CG MD scheme was benchmarked against atomistic MD to accurately represent the structure of a single spherical micelle of cetyltrimethylammonium chloride (CTAC) in water at varying concentrations of sodium chloride (NaCl) and sodium salicylate (NaSal) salts. This scheme provides a capability of performing MD on the order of microseconds for systems much larger in comparison to atomistic simulations, without the loss of relevant physical chemistry of surfactants and micellization behavior. These advantages of CG MD simulations were utilized to observe a first order sphere to rod transition of a CTAC micelle and to understand the mechanisms of such a shape transition, induced by NaSal salt above a threshold concentration[5]. Further, the CG MD scheme was applied in simulations of a binary system of spherical CTAC micelles to evaluate intermicelle potential of mean force (PMF)[6]. Effective interactions between charged self-assembled micellar structures as a function of salt concentration provide important details on how the addition of salt causes micelles to form larger/longer structures, starting from a spherical shape. To understand the mechanisms of flow-induced structure (FIS) transitions in surfactant solutions, non-equilibrium CG MD simulations of a single cylindrical micelle was first performed at varying shear rates to glean the effect of flow on micelle shape, orientation and rupture. Subsequently, binary interactions were studied under non-equilibrium (flow) conditions to identify how flow-alignment, end-to-end collision and merger of two micelles occur.

The CG MD scheme we have developed utilizes MARTINI CG potentials to describe CTAC, NaSal, and solvent (water) with a mapping of roughly 4 heavy atoms onto a single CG particle.[5, 6] For benchmarking purposes, systems prepared by utilizing the CG scheme were similar to atomistically detailed ones in terms of box dimensions and the molar ratios of constituent CTA^+ cations, Sal^- anions, Na^+, Cl^-, and water particles. Comparison between atomistic MD and CG MD was carried out at 9 different molar ratios of NaCl and NaSal salts. Simulations performed to determine structural properties were run for 15 ns in atomistic MD while they were half a microsecond in length for CG MD. Enhanced sampling of microsecond timescale in CG MD simulations enabled us to observe a salt-induced transition of a single spherical micelle in cylindrical shape. Molecular dynamics was performed in NPT ensemble at 300 K and 1 atm. Time step of dynamics was 2 fs in atomistic simulations while it was 33 fs in CG MD.

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Gromacs 4.0 molecular dynamics package was chosen because of the advantages it offers in terms of in-built choice of GROMOS-96 force field[10] for atomistic MD and readily available libraries of MARTINI force field, as well as, its highly optimized algorithm to run MD in parallel environments. Simulations were performed on IBM Bluegene/L supercomputer hosted by Brookhaven National Laboratory and an in-house cluster with 192 Intel Xeon processors.

CG MD simulations of a system of two micelles in an elongated box were performed to calculate the equilibrium PMF between the centers of two micelles using an umbrella sampling technique. Specifically, the centers of the two micelles were constrained by a harmonic potential with a minimum in potential at an initial separation of r_{min}=7.5 nm. The r_{min} of harmonic potential is slowly decreased from 7.5 nm to 4.0 nm (0.1 nm each time) after sampling 20 ns of MD at each constraining r_{min} separations. This allows micelles to gradually equilibrate as they approach from large enough separations like r_{min}=7.5 nm where they do not interact to contact separations (r_{min}=4.0 nm) where they fuse or interact strongly. The probability distribution at each constraining positions can provide the PMF $W(r)$ as a function of separation r as

$$W(r) = -k_B T \log p(r) - [-k(r-r_{min})^2]$$

where, k_B denotes Boltzmann's constant, T is temperature, $p(r)$ is probability distribution as a function of separation, k is the force constant associated with the umbrella potential, r_{min} is separation at which the umbrella potential displays a minimum. These simulations showed that aromatic anions such as Sal^- adsorb onto the positively charged micelle corona. As the salt to surfactant molar concentration ratio approaches unity, the micelle-water interface gets saturated with Sal^- anions with the aromatic ring penetrating into the hydrophobic micelle core and the negatively charged moiety reposing on the micelle surface. This renders the micelle-water interface nearly charge neutral. Under such conditions, two spherical micelles that approach each other were seen to readily exchange surfactant molecules and merge to form a stable cylindrical micelle[6]. In contrast, such merger was found to be nearly improbable in the presence of comparable amounts of simple salts such as NaCl since such salts dissociate into cationic and anionic entities in the bulk solvent.

Micelle dynamics were studied as a function of the Peclet number Pe and salt concentration. Flow-alignment was observed at O(1) values of Pe. The tumbling frequency was found to increase with increasing Pe as shown in Figure 1(a). For Pe >> 1, the micelle was found to break under flow-induced stresses: see Figure 1(b). It was found that for O(1) Pe and at sufficiently large amount of NaSal, collision between flow-aligned micelles results in exchange of surfactants through opening of their end-caps and merger of the two micelles to form a stable longer single cylindrical micelle. To our knowledge, this is the *first* molecular-level evidence in support of the FIS formation mechanism proposed by Turner and Cates [3].

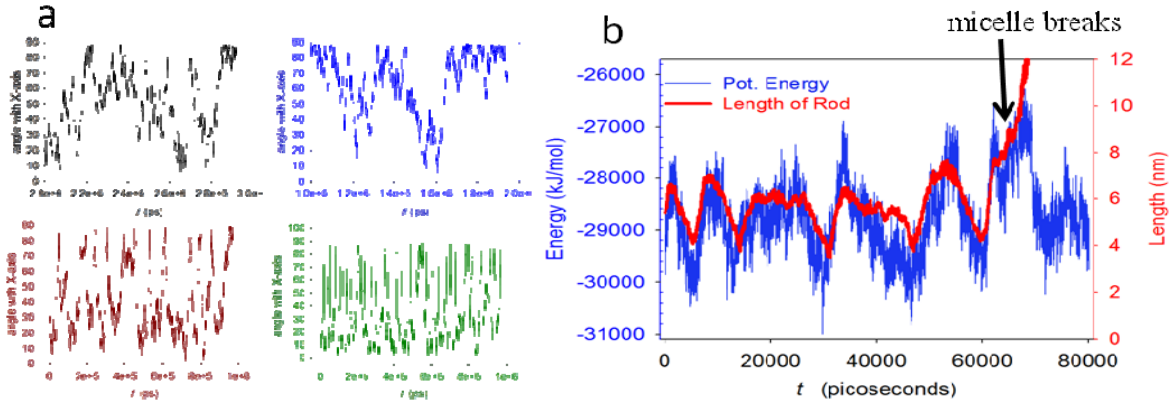

Figure 1(a): Tumbling cycles of a single CTAC micelle of length of approximately 5 nm for Peclet number Pe = 0 (equilibrium, black), 0.1 (blue), 10 (red) and 25 (green). An angle of zero degrees represents a flow-aligned state. As Pe is increased, flow alignment and tumbling events occur in a near-periodic fashion and more frequently. (b). Length and potential energy vs. time of a cylindrical CTAC micelle for Pe = 100. Flow-induced mechanical stresses are large enough to cause micelle rupture.

References

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