Structure, Dynamics and Rheology of Surfactant Micelle and Micelle-Nanoparticle Solutions from Molecular Dynamics Simulations

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Coarse grained molecular dynamics (MD) simulations [1-2], utilizing the LAMMPS MD simulation package, are used to study the equilibrium structure, shear-induced structure changes and rheology of cationic cylindrical micelle solutions. Systems that consist of up to a million coarse grained particles are simulated in the presence of explicit solvent and salt interactions. By varying the salt and surfactant concentrations, a phase diagram that consists of dilute, semi-dilute and entangled regimes is obtained. We also evaluate the micelle contours and orientation correlations from which micelle lengths, persistence length and shape anisotropy are calculated as functions of salt concentration. Addition of nanoparticles (NPs) to cationic wormlike micelles results in the formation of electrostatically stabilized micelle-NP junctions. The molecular mechanism and the kinetics of such junction formation will be elucidated. The effect of salt concentration and NP volume fraction on the structure and rheology of micelle-NP networks will be discussed. At sufficiently high salt concentrations, it is observed that branching in micelles results in a decrease in zero-shear viscosity of the solution. Non-equilibrium MD simulations are performed for micelle and micelle-NP solutions, showing shear thickening due to shear-induced structure (SIS) formation and shear thinning behavior depending on the salt and surfactant concentration. A shear-induced isotropic to nematic transition was observed for Weissenberg number Wi O(1), where Wi is defined as the product of shear rate and the intrinsic structure relaxation time of the system. For $Wi > 1$, micelles align in the flow direction. Mean square displacement of NPs in such solutions suggests that particles could undergo transient trapping due to entanglement constraints arising from the micelle structure.

1. A.V. Sangwai & R. Sureshkumar, Langmuir, 27, 6628 (2011)
2. A.V. Sangwai & R. Sureshkumar, Langmuir, 28, 1127 (2012)