Brownian Dynamics simulation of the viscoelasticity of wormlike micellar solutions

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Anionic surfactants are essential components of liquid formulations used in a wide range of applications such as personal care products. In aqueous solution and at concentrations higher than the first critical solution concentration, surfactants spontaneously self-assemble into micelles of spherical or rod-like (elongated) shape. The temperature, the surfactant concentration, and the presence of additional components are just a few of the factors that strongly influence the structure, dynamics, and functional characteristics of these systems. For example, above a threshold concentration, the addition of salt drastically changes the size and shape of the micelles, as spherical or rod-like surfactants aggregate to wormlike micelles (WLMs).[1] Simultaneously, the zero-shear viscosity of the solution increases by several orders of magnitude and goes through a maximum before it starts decreasing by further increasing the salt concentration.[2] It is thus clear that to design formulations with predefined rheological properties, a fundamental understanding of the relationship between composition, microstructure, and rheological response is needed.

In this work, we employ Brownian Dynamics (BD) simulations to address the rheology of such WLM solutions following the modelling scheme which, despite its simplicity, can effectively account for all key futures and interactions underlying the behaviour of these systems, such as the formation of entanglements between micelles and the "living" nature of micelles (i.e., the ability of surfactant assemblies to break and aggregate dynamically). In particular, the BD model employs two kinetic Monte Carlo (kMC) processes to simulate: a) the creation and destruction of micelles, as well as the slip of entanglements along the micelles backbones,[3] and b) the breakage and recombination of micelles.[4] Important model parameters (such as the bead size, the Kuhn length, and the solution compressibility) are calculated from lower all-atom or coarse-grained molecular dynamics (MD) simulations.[5] Emphasis in our study is given to the better understanding of the effect of these parameters on the simulation predictions for the morphological and rheological properties of the WLM solutions such as the micelle size distribution, the zero-shear rate viscosity, and the spectra of storage and loss moduli. We are also interested in how these parameters relate to specific physicochemical and thermodynamic conditions of the solution such as the salt concentration, the presence of co-surfactants or polymers, and the temperature.

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