Modelling the Self-Assembly of a Model Cationic Surfactant by Lattice Monte Carlo Simulations

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Above the critical micellar concentration (*cmc*), surfactants with the right solvophobic/solvophilic ratio, are able to self-assemble and form aggregates. At the *cmc*, the concentration of free surfactants in solution stops increasing, whereas that of aggregates starts to increase. Depending on several conditions, such as temperature, solvent, electrolytes, cosurfactants, and on the surfactant architecture as well, the *cmc* can vary rather significantly as well as the shape and size of micelles at equilibrium.[1] Due to their large applications in formulation chemistry and in nanotechnology as templates for the synthesis of advanced materials, the principles controlling self-assembly and micellization of surfactants are of fundamental relevance. In the last decades, computer simulations have played a key role in determining the phase and aggregation behavior of many different amphiphilic systems,[2] via the implementation of both rigorous atomistic[3,4] and coarse-grained (CG)[5−7] models.

In this work, by performing lattice Monte Carlo (MC) simulations, we investigate the self-assembly of a cationic surfactant (ricinoleamidopropyltrimonium methasulfate) which finds large applications in formulation chemistry and, more specifically, in cosmetics. We apply an efficient CG model[7] where the surfactant molecules are represented as linear chains of connected beads in a three-dimensional lattice network. The headgroups, carrying the charge, are neutralized by a number of monovalent counterions. The charged groups interact via a Coulombic potential and a hard core repulsion, whereas neutral tail-tail interactions are only established between close neighbors, defined by the lattice coordination number. All the lattice sites are occupied by the surfactant or by the solvent. By tuning the mutual interaction between the solvophilic and solvophobic groups, and that between them and the solvent, we are able to observe aggregation and formation of micelles. We compute the *cmc*, the density distribution profiles in the micelles and their aggregation number, and estimate the dependence of these parameters on temperature.

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