Free energy, aggregation number, counterion binding, and transport properties of micelles in surfactant solutions via Monte Carlo simulations

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Analytical approaches based on mean-field models of the work of aggregation have been successful in thermodynamic and kinetic description of micellization in surfactant solutions [1]. Nevertheless a verification of these theoretical models by means of computer simulations may help to improve them and provide links between the theory and experiment. An implicit solvent model is taken to investigate thermodynamic, e.g. an aggregation work, and structural properties of surfactant solutions using Monte Carlo method. A number of hard core molecular chains possessing charged and neutral monomers and a number of free counterions are placed to the dielectric continuum medium and represent an ionic surfactant solution. In the case of nonionic surfactant, two monomers of a chain carry positive and negative charges and make a dipole that represents a head of an amphiphilic molecule. The uncharged monomers of the chain form the hydrophobic tail and interact with each other via an effective short range potential. A special attention is paid to the proper choice of the potentials of interaction of the monomers since they play a crucial role in the simulated self-assembly. The work of aggregation of a micelle can be found if the equilibrium distribution of the micelles as a function of the aggregation number is known [2]. We use the standard Monte Carlo method [3] in order to obtain this distribution. A study of the mixtures of the micelles of different shapes (spherical, cylindrical, etc.) makes it necessary to consider a wide range of surfactant concentrations. Within a modification of the entropic sampling Wang-Landau approach [4], the free energy of the micellar system (as well as other thermodynamic and transport characteristics) as a function of surfactant concentration is obtained.

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