

Abstract

In this study the primary formation kinetics of the self-assembly processes of surfactant molecules into spherical aggregates in oil-rich microemulsions are studied, starting from an unstructured stock solution of non-ionic surfactant in a short-chained oil which is rapidly mixed with a polar phase. Microemulsions can be studied as simple physical membranes allowing variations of its properties by changes in the composition and the integration of either low-molecular or polymeric molecules, representing membrane building blocks. Systematic static and time-resolved small angle neutron scattering, as well as transmission and light scattering experiments combined with a new temperature-stable ultra-fast stopped-flow setup were performed to determine the size of the microstructure and its structural evolution. Remarkably, in all investigated systems the internal interface is already present after the instrumental dead time of 20 ms which is followed by a structural evolution. The microemulsion droplets grow in size at the expense of dispersed emulsion droplets that result from the high shear mixing process. To simulate the crowded environment in natural membranes, small amounts of an amphiphilic, asymmetric diblock-copolymer poly(ethylene-*co*-propylene)-*block*-poly(ethylene oxide) were added to the oil-rich, non-ionic microemulsion. This additive increases the elastic moduli and significantly slows down the kinetics. Differently, small molecules such as low-molecular fragrance additives show an alteration of the membrane properties, but can either improve or inhibit the efficiency and the structure formation depending on the intermolecular interactions within the surfactant monolayer. The addition of anionic sodium dodecyl sulfate accelerates the formation kinetics due to charge distribution. As a result, the microemulsion reaches equilibrium within few hundreds of milliseconds. Additionally, increasing the surfactant chain length (and thereby lowering the interfacial tension and increasing the bending elasticity) also results in faster relaxation times due to stronger intermolecular interactions in the surfactant layer and a more pronounced hydrophobic effect. Mixing the corresponding water-rich microemulsion along different pathways revealed that if the surfactant is already solubilized within the dispersed phase and mixed with the continuous medium, no kinetics are resolvable meaning the formation of the final microstructure is instantaneously completed.