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Observing Assembly Processes in Colloidal Systems by Means of Stopped-Flow Experiments – Soft Matter in Motion

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Self-assembled systems composed of surfactants, copolymers, and/or polyelectrolytes exhibit a large variety of different structures in aqueous solution that depend in a subtle way on the molecular structure of the components, the composition of mixtures, concentration, and external parameters such as pH, ionic strength, temperature, etc.

The formation of such self-assembled structures is typically a highly dynamic process, but one where the typical time scales for structural changes can vary largely from nanoseconds to weeks and months. In many situations morphological changes in amphiphilic systems can be triggered by mixing with other surfactants, additives, or solubilisates. In our experiments, we concentrated on the time range of ms to many mins, a time range that can be studied well by means of the stopped-flow technique. Such experiments can be done in the lab by employing turbidity, conductivity, fluorescence, or DLS as detection methods. However, they can also be coupled to high-flux SANS/SAXS instruments, which allow to obtain detailed structural information in the size range of 1-1000 nm, with a time-resolution of 5-50 ms.

With this approach a variety of different morphological transitions was investigated, e.g. the formation of unilamellar vesicles or lamellar phases by mixing oppositely charged surfactant or adding a cosurfactant, as well as the solubilisation of hydrophobic compounds in micellar solutions, leading to micro- or nanoemulsions. Such processes like the formation of monodisperse unilamellar vesicles take place in a way purely governed by diffusion. In the particular case of vesicle formation, they proceed either via disk-like or rod-like intermediates. Their formation as well as further ageing processes can be described by means of the bending energy of the respective bilayers. The structural progression of such systems can be modelled by simple simulations which allow to understand the ageing processes in terms of simple coalescence processes. For the case of oil solubilisation clear correlations between the type of oil and surfactant can be observed. Finally, also the case of formation of interpolyelectrolyte complexes was studied, which depends largely on the type, but also Mw of the polyelectrolytes studied and can proceed via a number of different transformational steps.

In summary, the kinetics of self-assembly is typically much more complex and variable than their phase behaviour and can vary largely with respect to their time scales. It is very important for understanding the properties and can also be central to structure formation, if that is kinetically controlled.

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