Resolving Hierarchical Self-Assembly Pathways of Oppositely Charged Surfactants using Stopped-Flow Time-Resolved (U)SAXS

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Fluorinated compounds have been detected in various ecosystems, from aquatic environments to agricultural soils, and even in wildlife (Evich et al., 2022). Their persistence in the environment can be highly detrimental, with a growing body of evidence linking them to adverse effects in life, including humans (Jagani et al., 2025). Consequently, strategies to remove these compounds from water are urgently needed. A promising approach is to exploit their precipitation via catanionic association in water. In this case, mixing oppositely charged surfactants, even below their individual critical micellar concentrations (CMCs), can lead to rapid molecular association, followed by microstructure formation and precipitation from the aqueous medium (Weiss et al., 2008; Hörmann et al., 2023). However, the transient microstructures and the kinetic pathways that lead to their formation remain only partly known (Gradzielski, 2003; Weiss et al., 2008). In this work, we investigate the time-resolved self-assembly kinetics of equimolar sodium perfluorooctanoate (NaPFO) and octyltrimethylammonium bromide (OTAB) below their CMC, using stopped-flow mixing coupled with time-resolved ultra-small- and small-angle X-ray scattering (TR-(U)SAXS). Data analysis is performed by employing a physically constrained hierarchical scattering model. The results suggest a hierarchical assembly scenario, in which the surfactants organise into composition-dependent unilamellar vesicles, with bilayer composition that may show leaflet asymmetry (Hörmann et al., 2023). The vesicles then associate into polycondensates (Takahashi et al., 2017), which remain correlated via inter-polycondensate electrostatic interactions. This approach, opposite to traditional phenomenological fitting methods, allows for assessing structurally meaningful, time-dependent observables. These include mean vesicle radius, vesicle number density, average aggregation number per polycondensate, bilayer leaflet composition, and the distribution of surfactant between free and associated states. Based on this structural analysis, a kinetic model based on mass-balance relations and rate equations is developed. This connects the SAXS-derived time-dependent observables to potential concurrent growth routes, allowing one to understand whether increases in vesicle size result from surfactant uptake from the free monomer pool, coalescence within polycondensates, or a combination of both processes. We then provide closed-form predictions for the coalescence-only scenario and a regression-based approach for estimating kinetic coefficients in the mixed-growth case. Overall, this work shows how TR-(U)SAXS links hierarchical self-assembly to microscopic kinetic insights in dynamically assembling soft-matter systems. Additionally, it offers a mechanistic understanding relevant to the catanionic capture of fluorinated surfactants from water.

Keywords:
Hierarchical self-assembly; catanionic surfactants; stopped-flow TR-(U)SAXS; self-assembly kinetics; water remediation

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