Dynamic partitioning of surfactants into non-equilibrium emulsion droplets analyzed by quantitative Mass Spectrometry

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Abstract

Characterizing the distribution of molecules between fluid phases is essential for understanding chemical concentrations in heterogeneous mixtures. While partitioning is typically studied under equilibrium conditions, some mixtures may exist in multiple phases only when out-of-equilibrium. Oil-in-water emulsion droplets stabilized by surfactants are an example of such non-equilibrium systems. These droplets are thermodynamically unstable and gradually dissolve or solubilize over time. Consequently, equilibrium properties may not accurately describe the behavior of these droplets.

This study investigates the partitioning of nonionic surfactants between microscale oil droplets and water under non-equilibrium conditions. Using quantitative mass spectrometry, the composition of individual micro-droplets is analyzed over time with varying surfactant composition, concentration, and oil molecular structure. Nonionic surfactants rapidly partition into oil micro-droplets, reaching a non-equilibrium steady-state concentration significantly higher than in the aqueous phase. Over hours, droplets solubilize, releasing surfactants back into the water, leading to transiently high concentrations near the oil-water interface. This results in localized microemulsion phases and low interfacial tension.

Since emulsions are widely used in industries such as oil recovery, pharmaceutical formulation, food, and cosmetics, understanding their behavior is crucial. These emulsions typically exist in a non-equilibrium state prior to phase separation, where traditional equilibrium partitioning coefficients are no longer representative. The partitioning dynamics revealed in this study provide insights into emulsion stability, wetting dynamics, and more. This knowledge is essential for industries to optimize the functionality of surfactant-stabilized emulsions, enhancing their application and performance in various products and processes.