Emulsifier Saturation Modulates Interfacial Monoglyceride Crystallisation and Polymorphic Transitions

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Monoglyceride crystals play a critical role in stabilising food emulsions through their interfacial activity at oil-water interfaces. However, the presence of co-emulsifiers can significantly alter monoglyceride crystallisation behaviour, with effects that vary depending on emulsifier molecular structure. This study investigates how emulsifier saturation influences the interfacial crystallisation of glycerol monostearate (GMS) using a powerful combination of Profile Analysis Tensiometry (PAT) and synchrotron-based Small- and Wide-Angle X-ray Scattering (SAXS/WAXS). Two polysorbate emulsifiers with identical C18 chain lengths but differing saturation: Polysorbate 60 (Tween® 60, fully saturated) and Polysorbate 80 (Tween® 80, monounsaturated), were compared at an isolated oil-water interface. PAT measurements revealed that Tween® 80 significantly inhibited GMS crystallisation, delaying the onset of interfacial crystal activity to 13.8 °C compared to 16.5 °C with Tween® 60. Synchronised SAXS/WAXS analysis captured the structural evolution of interfacial GMS crystals in real-time, revealing a polymorphic transition from sub-α to β prime phase that increased crystal hydrophobicity. These findings demonstrate that even subtle differences in co-emulsifier structure, specifically the presence of a single double bond, can profoundly affect the temperature, kinetics, and polymorphic behaviour of interfacial lipid crystallisation. This integrated PAT-SAXS/WAXS approach provides unprecedented insight into interfacial crystallisation dynamics and offers a powerful framework for rational emulsion design in food systems.

Keywords:
Interfacial crystallisation, monoglycerides, polysorbates, PAT, SAXS/WAXS, emulsion stability, polymorphism