Predicting random jamming-induced repulsive gelation in sodium caseinate-stabilized polydisperse nanoemulsions by combining the entropic, electrostatic, interfacial and steric interactions

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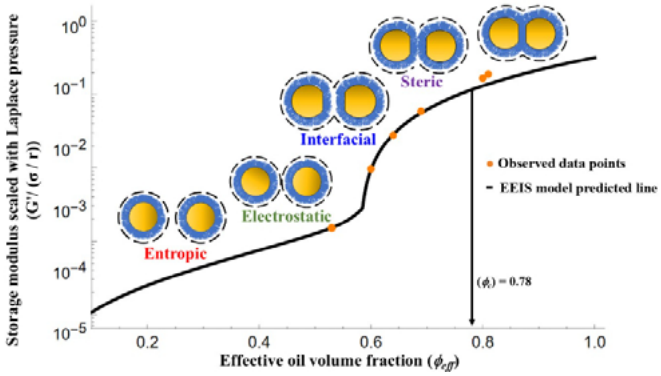
Repulsive emulsions exhibit a progressive transition from viscous liquid to viscoelastic gel states as the oil volume fraction (ϕ) increases [1]. These transitions arise from inter-droplet interactions involving entropic, electrostatic, interfacial, and steric forces as the droplets come close to each other with a progressive increase in ϕ . In ionic small molecule emulsifier-stabilized monodisperse emulsions, the balance among these contributions can be determined using the Entropic–Electrostatic–Interfacial (EEI) model developed by Kim et al. [2]. The EEI model predicts the critical volume fraction (ϕ_c) for maximal random jamming (ϕ_{MRJ}), where the repulsive oil droplets are close-packed, leading to a sudden change in their rheology and the formation of an elastic gel. In this study, the EEI model was extended to include steric repulsion, resulting in the Entropic–Electrostatic–Interfacial–Steric (EEIS) framework. To validate the model, sodium caseinate-stabilized nanoemulsions ($d_{3,2} \approx 271$ nm, relative polydispersity 0.61) were prepared using high-pressure homogenization and size-fractionated through three-step ultracentrifugation to obtain pseudo-monodisperse emulsions with a range of droplet sizes and polydispersity. Results showed that elasticity increased with increasing ϕ due to droplet crowding, leading to ϕ_{MRJ} [3]. Moreover, smaller droplets exhibited higher elasticity, shifting the ϕ_{MRJ} to a higher value, attributed to the increase in effective oil volume fraction (ϕ_{eff}) resulting from the greater interfacial shell layer thickness from the combined effects of the steric barrier and its surrounding electrostatic charge cloud [4]. The EEIS model predicted the transition of normalized elasticity (G′ scaled with Laplace pressure) as a function of ϕ (Figure 1). The Figure shows that, at low ϕ (<0.5), the system was dominated by entropic forces arising from thermal motion and excluded volume effects. With increasing crowding ($\phi \approx 0.55–0.6$), the electrostatic contribution sharply increased, followed by interfacial interactions ($\phi \approx 0.6–0.78$), marking the transition from a liquid-like to a glassy state. Beyond the critical jamming point ($\phi_c \approx 0.78$), steric interactions emerged as the dominant repulsive force due to overlap of adsorbed steric layers, leading to a steep rise in G'_p and the formation of an elastic gel. The results of the model will be used to understand the jamming transition of polydisperse emulsions and establish a relationship between ϕ_c and polydispersity. These findings will enhance understanding of the role of droplet size distribution in the formation and tailoring of protein-stabilized emulsion gels, providing new insights for food structuring and soft matter design.



Storage modulus scaled with Laplace pressure (G′/(σ/r)) as a function of effective oil volume fraction (ϕeff), showing the transition of entropic-electrostatic-interfacial-steric regime, with predicted critical jamming point (ϕc ≈ 0.78).

References:

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