Hydrogen bonding versus electrostatic screening in saponin-stabilised interfaces: molecular origins of foam stability

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Understanding how intermolecular interactions govern the structure and mechanics of biosurfactant interfaces is essential for the rational design of sustainable foams and emulsions. Here, we investigate how hydrogen bonding and electrostatic interactions modulate the interfacial organisation and foaming behaviour of Quillaja saponin systems in the presence of small, water-soluble additives.

Using a multi-scale experimental and computational approach combining surface tensiometry, interfacial dilational rheology, foam stability measurements, vibrational sum-frequency generation (SFG) spectroscopy, electrokinetic analysis, and atomistic molecular dynamics (MD) simulations, we identify distinct, additive-specific mechanisms that control interfacial structure and performance.

Despite negligible intrinsic surface activity of the additives, profound changes in interfacial mechanics and foam stability are observed. Glycerol, acting as a hydrogen-bond promoter, enhances interfacial cohesion and increases dilational elasticity up to ~200 mN m^{-1}, leading to significantly improved foam stability. In contrast, urea disrupts cooperative hydrogen-bond networks, weakens interfacial elasticity, and accelerates foam decay. Choline chloride induces strong electrostatic screening, reduces interfacial charge, and lowers surface elasticity, while simultaneously promoting large aggregate formation that contributes to intermediate foam stability via Pickering-like effects.

SFG spectroscopy reveals that these macroscopic trends originate from additive-induced reorganisation of interfacial water and saponin headgroups. Glycerol reduces the fraction of strongly hydrogen-bonded interfacial water while reinforcing lateral cohesion, whereas urea redistributes hydrogen-bond populations and disrupts headgroup interactions. Choline chloride strongly suppresses interfacial OH response, consistent with charge neutralisation and reduced interfacial electric fields. MD simulations confirm the formation of dynamic, short-lived additive–saponin associations and highlight the dominant role of collective intermolecular interactions rather than specific complexation.

Our results demonstrate that foam stability in saponin systems is not governed by surface activity alone but is controlled by the interplay between hydrogen-bond networks and electrostatic interactions within the interfacial layer. These findings provide a mechanistic framework for designing bio-based formulations with tunable interfacial properties and enhanced performance in pharmaceutical, cosmetic, and industrial applications.

Keywords:
Saponin; Hydrogen bonding; Electrostatic interactions; Surface activity; Interfacial dilational rheology; Foam stability; Biosurfactants;

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