Building blocks with tunable electrostatic interactions at the gas/liquid interface as a driving force for macroscopic foam stability and structure

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Foams are of enormous importance as we find them in many applications. For that reason, it is of great interest to determine molecular building blocks that drive macroscopic foam properties through their entire hierarchical chain. As gas/fluid interfaces are ubiquitous within foam, it is particularly important to study their microscopic properties on a molecular level. This includes not only the molecular structure and coverage of surface active species, but also their charging state at the interface as well as the structure of solvating interfacial water molecules [1-4].

Using a unique combination of interface specific vibrational sum-frequency generation (SFG) and complementary analytical methods (ellipsometry, tensiometry, surface dilatational rheology) [1-4], we have identified a molecular building block at air/water interfaces and provide new information on the adsorption behaviour of macromolecules and their complexes with low molecular weight surfactants.

Specifically, we relate molecular structures of air/water interfaces that are modified by different mixtures of macromolecules (β-lactoglobulin proteins as well NaPSS polyelectrolytes), surfactants (SDS, CTAB) and by different electrolyte properties (pH, ionic strength) to the structure and stability of macroscopic foam. By changing the former bulk properties different charging conditions and lateral interactions of molecules at air/water interfaces are realized and were measured with vibrational SFG. We demonstrate that interfaces with thick and aggregated layers of molecules that have negligible electrostatic interactions and dominating attractive interactions lead to a (local) maximum in macroscopic foam stability. This is shown to be independent of the macromolecule's chemical identity (proteins [1-5] or NaPSS polyelectrolytes [6]). We therefore propose that the latter is a microscopic building block that can be used to tailor foam properties such as structure and stability in a targeted way.

However, considering earlier studies on foam films (single lamella experiments) which show that electrostatics can stabilize foam films via repulsive interactions between the two approaching air/water interfaces. We come to the conclusion that there must be additional hitherto unresolved stabilizing elements such a blocking effect of aggregates in plateau borders or stabilization by crosslinking of foam film interfaces with (large) aggregates. These open questions are to be addressed in future experimental investigations.

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