

Structure, thermodynamics and rheology of proteins and polymers at air-water interface

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Complex fluid-fluid interfaces are common to living systems, foods, and personal and biopharmaceutical products. They occur wherever surface-active molecules like polymers, proteins and particles accumulate at fluid interfaces. In general, these complex fluid–fluid interfaces exhibit complex thermodynamic, structural, and rheological behaviors that differ substantially from those observed in bulk environments. Understanding these interfacial phenomena is important for applications involving polymer thin films, foams, emulsions, coatings, and biopharmaceutical formulations. The overarching goal of this work is to expand the understanding of molecular behavior of surface-active materials confined at the air–water interface compared with their behavior in solution. Particularly, structure–property relationships of insoluble glassy polymers and soluble monoclonal antibodies (mAbs) adsorbed at the air–water interface are investigated, revealing how interfacial confinement and interfacial flow affects structure, thermodynamics, and rheology of these materials.

The properties of insoluble monolayers at the air-water interface of a high T_g polymer poly (methyl methacrylate) PMMA ($T_g = 109^\circ\text{C}$) and a low T_g polymer poly (n-butyl methacrylate) PnBMA ($T_g = 30^\circ\text{C}$) are studied. PMMA, the high T_g polymer, exhibits much higher surface moduli than PnBMA across all measured surface concentrations. With increasing surface concentration, both polymers show a transition from a viscous-dominated regime to an elastic-dominated regime. The temperature dependence of the oscillatory dilatational moduli measured for a highly compressed monolayer revealed a reduction in the apparent 2D glass transition temperature of the quasi-2D film for PnBMA compared to its bulk value. NR measurements showed that differences in hydration and interfacial packing between PnBMA and PMMA strongly influence their mechanical response, highlighting the role of polymer–water interactions in governing insoluble film mechanics.

For the soluble protein interfaces, a monoclonal antibody film at the air-water interface is studied under both quiescent and stressed conditions. Classical kinetics model using the Ward–Tordai framework coupled with the Frumkin equation of state cannot capture the surface pressure evolution of mAb adsorption. Under small deformations, mAb interfaces exhibited highly elastic, soft glassy behavior with weak frequency-dependent shear and dilatational responses. Under large deformation, XRR revealed compression-induced densification, molecular reorientation, and partial desorption. Correlations between structure and rheology showed that the interfacial elastic modulus scales strongly with the volume fraction of a dense hydrophobic region in close proximity to the air phase, suggesting a link between nanostructure and macroscopic mechanical response.

Furthermore, mAb interfacial properties are shown to have a strong correlation to their long-term stability. Surface pressure and interfacial shear moduli of five antibodies are correlated with the number of visible particles in solution after a three-year stability study. Antibodies that formed more elastic and densely packed interfacial films showed greater particulate formation during storage. XRR further showed that the development of a hydrophobic interfacial region correlates with both interfacial elasticity and long-term instability. These results suggest that interfacial rheological and structural measurements can provide mechanistic insight and may serve as important metrics for predicting mAb formulation stability.

Overall, this work advances the understanding of complex fluid interfaces by characterizing two distinct interfacial systems: insoluble polymer Langmuir films and soluble protein Gibbs layers. The comprehensive thermodynamics, rheology, and molecular structure characterization provides insight into the behavior of different classes of material at air-water interface. These results may have important implications on material selection and the rational design of interfacial systems.