

453h Dynamic Biomolecular Interactions at the Aqueous Interface with Compressed and Supercritical Fluids

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The dynamic surface activity of lysozyme and dipalmitoyl phosphatidylcholine (DPPC) vesicles at the aqueous interface with compressed and supercritical fluids are examined via high-pressure interfacial tension measurements using the pendant drop technique. The density and interfacial tension in compressible fluid systems varies significantly with pressure, providing a versatile medium for elucidating interactions between biomolecules and fluid interfaces, and a method to elicit pressure-dependent interfacial morphological responses. Investigating surface activity of biomolecules is motivated in part by recent advances in more benign compressed and supercritical fluid technologies for liposome synthesis, enzyme purification, biocatalysis, and sterilization.

The effects of lysozyme concentration (0.0008, 0.01, and 1 mg/l) and pressure (≥ 7 MPa) on the dynamic surface response in the presence of ethane, propane, N₂, and CO₂ at 298 K are examined. Rapid interfacial lysozyme adsorption reduces the induction phase and quickly leads to interfacial tensions consistent with protein conformational changes and monolayer saturation at the compressed fluid interfaces. Protein adsorption, as indicated by surface pressure, correlates with calculated Hamaker constants for the compressed gases, denoting the importance of dispersion interactions. Lysozyme diffusion coefficients from the bulk aqueous phase to the fluid interface are examined and compared to previous works with conventional organic solvents. For DPPC at aqueous/supercritical CO₂ interfaces (1.8 to 20.7 MPa, 308 K), 2 to 3-fold reductions in interfacial tension were observed relative to the pure binary fluid system. The resulting surface pressures are consistent with liposome adsorption/destabilization at the CO₂ interface and pressure-dependent morphological changes within the resulting DPPC monolayer. Transient DPPC surface pressure behavior was most noticeable at 3.5 MPa CO₂, which, based on previous studies using fluorescence spectroscopy, is near the liquid-condensed/liquid-expanded DPPC phase transition. Specific focus will be given to describing enzymatic and lipid vesicle interactions using interfacial and colloidal theory.