Dynamical and rheological properties of fluorinated surfactant films adsorbed at the pressurized CO2-H2O interface

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The dynamics of adsorption, interfacial tension, and rheological properties of two phosphocholine-derived partially fluorinated surfactants FnHmPC, designed to compensate for the weak CO(2)-surfactant tail interactions, were determined at the pressurized CO(2)-H(2)O interface. The two surfactants differ only by the length of the hydrocarbon spacer (5 CH(2) in F8H5PC and 11 CH(2) in F8H11PC) located between the terminal perfluoroalkyl chain and the polar head. The length of this spacer was found to have a critical impact on the adsorption kinetics and elasticity of the interfacial surfactant film. F8H5PC is soluble in both water and CO(2) phases and presents several distinct successive interfacial behaviors when bulk water concentration (C(W)) increases and displays a nonclassical isotherm shape. The isotherms of F8H5PC are similar for the three CO(2) pressures investigated and comprise four regimes. In the first regime, at low C(W), the interfacial tension is controlled by the organization that occurs between H(2)O and CO(2). The second regime corresponds to the adsorption of the surfactant as a monolayer until the CO(2) phase is saturated with F8H5PC, resulting in a first inflection point. In this regime, F8H5PC molecules reach maximal compaction and display the highest apparent interfacial elasticity. In the third regime, a second inflection is observed that corresponds to the critical micelle concentration of the surfactant in water. At the highest concentrations (fourth regime), the interfacial films are purely viscous and highly flexible, suggesting the capacity for this surfactant to produce water-in-CO(2) microemulsion. In this regime, surfactant adsorption is very fast and equilibrium is reached in less than 100 s. The behavior of F8H11PC is drastically different: it forms micelles only in the water phase, resulting in a classical Gibbs interface. This surfactant decreases the interfacial tension down to 1 mN/m and forms a strongly elastic interface. As this surfactant forms a very cohesive interface, it should be suitable for formulating stable water-in-CO(2) emulsions. The finding that the length of the hydrocarbon spacer in partially fluorinated surfactants can drastically influence film properties at the CO(2)-H(2)O interface should help control the formation of microemulsions versus emulsions and help elaborate a rationale for the design of surfactants specifically adapted to pressurized CO(2).