Rich interfacial films formed from aggregates in α-cyclodextrin solutions

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Cyclodextrins (CDs) are cyclic oligosaccharides formed by six (α), seven (β), or eight (γ) 1,4-linked α-D-glucopyranoside units. They are probably the first family of molecules that spring to mind when one looks to encapsulate small hydrophobic species [1]. CDs meet a number of characteristics that are not easy to bring together in a family of compounds, namely low toxicity, biocompatibility, chemical stability, and ease of synthesis and purification [2,3] Additionally, CDs are good targets for chemical modifications, which can enhance further their various attributes [4]. Nevertheless, the fundamental behavior of CDs in aqueous solutions and at interfaces is not yet fully understood.

In the present work [5], the spontaneous aggregation of α-CD molecules in aqueous solution and the interactions of the resulting aggregates at the liquid/air interface have been studied at 283 K and 298 K using a battery of experimental techniques: transmission electron microscopy, dynamic light scattering, isothermal titration calorimetry, surface tensiometry, Brewster angle microscopy, neutron reflectometry and ellipsometry. We show that molecules spontaneously form aggregates in the bulk that grow in size with time. These aggregates adsorb to form films at the water/air interface with their size in the bulk determining the adsorption rate. The material that reaches the interface coalesces laterally to form two-dimensional organized domains on the micrometer scale with a layer thickness on the nanometer scale. These processes are affected by the ages of the bulk and the interface and the temperature. The resulting film morphology is locked in a kinetically-trapped state. Our results reveal a surprising complexity of the parallel physical processes taking place in what might have seemed at first like a rather simple system.

Figure. (left) Dynamic light scattering data for fresh and aged α-CD solutions both at 283 and 298 K; (Right) Ellipsometry data showing the adsorption of aggregates under the same experimental conditions – in this case the lateral inhomogeneities results from patches of α-CD moving in and out of the laser beam by Brownian motion.