

P.20 Direct effects of non-equilibrium aggregates on Pdadmac/SDS layers at the air/water interface

R A Campbell¹, M Yanez Arteta^{1,2}, T Nylander², B A Noskov³ and I Varga⁴

¹Institut Laue-Langevin, France, ²Department of Physical Chemistry, Lund University, Sweden, ³Chemical Faculty, St. Petersburg State University, Russia, ⁴Institute of Chemistry, Eötvös Loránd University, Hungary

The exploitation of non-equilibrium effects in oppositely charged polyelectrolyte/surfactant (P/S) mixtures is attracting more and more attention.[1-3] Here we discuss various different mechanisms to explain the non-equilibrium properties of P/S mixtures at the air/water interface in terms of adsorption vs. trapping or spreading of particles delivered by convection[4] vs. deposition under gravity.[5] Poly(diallyldimethylammonium chloride)/sodium dodecyl sulfate (Pdadmac/SDS) samples have been examined with respect to the bulk composition, changes in the bulk phase behavior and sample history using ellipsometry, neutron reflectometry and Brewster angle microscopy (BAM). Aggregate penetration into the adsorption layer is observed from kinetically-trapped particles at the edge of the phase separation region for *fresh-mixed* samples. For the supernatant of well-equilibrated *aged-settled* samples, penetration of aggregates occurs only when the particles are positively charged, which is attributed to their interaction with the negatively charged headgroups of the surfactant monolayer. Through the application of a light mechanical stress to the sediment, the surface properties of *aged-redispersed* samples are significantly modified, and the change in the interfacial properties is again faster for samples with positively charged aggregates. Trapping of particles at the interface occurs for samples where the surface is not subjected to cleaning by aspiration, and the process is most prevalent at compositions close to charge neutralization (0.82 mM; see figure). This work begins to outline the complexity of how non-equilibrium P/S aggregates can dramatically impact the interfacial properties directly. The implications of our findings are discussed in terms of material applications.

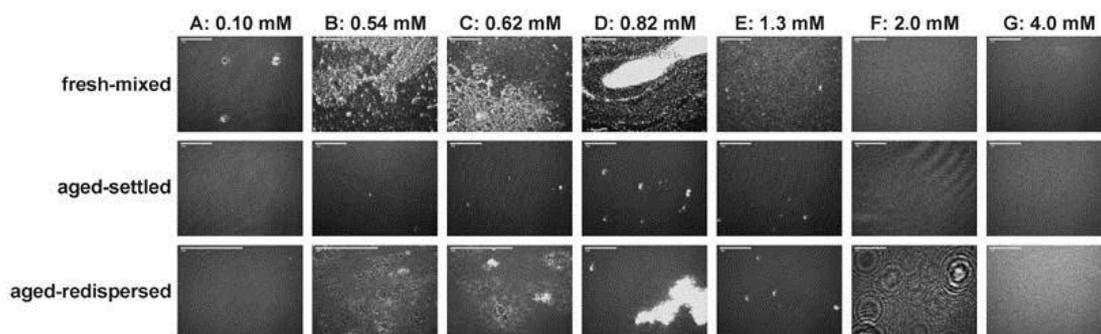


Figure. BAM images of *fresh-mixed*, *aged-settled* and *aged-redispersed* 100 ppm Pdadmac/SDS samples in 0.1 M NaCl without surface cleaning by aspiration. The scale bars are all 100 μm .

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