Dominant Influence of Non-equilibrium Effects in Oppositely Charged Polyelectrolyte/Surfactant Mixtures at the Air/Water Interface

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Oppositely charged polyelectrolyte/surfactant mixtures control the properties of many of the consumer products that we use every day. While work has been carried out to understand the properties of these mixtures under dynamic conditions relevant to processing and applications [1–2], there is a growing awareness that also the static properties of such mixtures are strongly influenced by non-equilibrium effects [3–4]. Even so, the current physical models for these mixtures at the static air/water interface are set in a framework of chemical equilibrium [5–6]. We have worked recently to relate the interfacial properties of these systems to different non-equilibrium processes in the bulk and at interfaces [7–12].

Here we demonstrate that non-equilibrium effects dominate the interfacial properties of such mixtures. Our work focuses on the strongly interacting systems Pdadmac/SDS and NaPSS/DTAB measured using a range of bulk and surface techniques including neutron reflectometry, ellipsometry and Brewster angle microscopy. We show that the extremely slow equilibration of the bulk means that these materials inevitably exist out of equilibrium conditions even if steady state interfacial properties can be measured in the meantime. The situation is further complicated by the irreversible formation of liquid crystalline particles in the bulk which can be immune to dissolution upon chemical change. The formation of these particles depletes the bulk solution yet their penetration into the interfacial layer modifies the macroscopic interfacial properties in different ways, e.g. their retention at the interface affects the rheological properties while their dissociation and spreading of material by Marangoni flow affects the surface tension. The mechanism of penetration of the particles into the interfacial layer is also mediated by different parallel processes such as surface affinity, kinetic trapping and transport under gravity. The static interfacial properties of planar surfaces, droplets and foams are therefore necessarily all different, and these factors need to be taken into account in future physical models.