

Did you know.....? series for March/April 2021

Did you know.....how surfactants are distributed within the latex? As we all know, the surfactants we add to synthetic latexes have allowed us to create wonderful nanoparticles and at the same time to provide colloidal stability (against salts, freezing/thawing and mechanical shear) to the dispersions. But they also can cause foaming problems when mixing and transporting the latexes, and remain in the final products causing potential water absorption problems in films and coatings. However, on a commercial scale, they are necessary. Perhaps it goes without saying, but it should be obvious to us that the surfactants will be distributed between the water phase and the particle surface, and the question then arises as to what that distribution looks like. But first, are the surfactants also inside the polymer particles? For anionic or cationic surfactants, the answer is a resounding no. In fact, common anionic surfactants like sodium dodecyl sulfate (SDS, or SLS) are not even soluble in the monomers we use to make the polymer. Non-ionic surfactants present a different situation as some are soluble in the monomers we choose, but not usually soluble in the final polymers. This results in the potential condition that when non-ionics are added to a batch polymerization (lots of monomer in the particles) some of that surfactant might become absorbed inside the particle in the early stages of the polymerization, and perhaps get trapped within the particles in the latter part of the polymerization. Certainly, there are some complexities here. But for the anionic (or cationic) surfactants, the situation is simpler. Here we only have to ask how the surfactant distributes between the water and the particle surface. It is clear that when the surfactant concentration in the water phase is at its critical micelle concentration (CMC), surfactant on the particle surface must be packed to its maximum spatial density (i.e. any more surfactant added to the latex would just form more micelles). This CMC condition allows us to measure how much of the total surfactant is on the surface of the particles at maximum packing. That number is commonly designated as AS, with units of \AA^2 of particle surface area per surfactant molecule. This value is known to vary with the type of polymer at the surface of the particle – the more polar the polymer, the higher the AS value (meaning less densely packed). Now consider the situation in the figure below where we have imagined a composite particle with 2 polymers of differing polarities, each presenting its own surface to the water phase. One can see here that at a fixed level in the latex, the surfactant is distributed between the

water and both polymer surfaces at the same time, all conditions being at some thermodynamic equilibrium. This interesting situation, at all levels of surfactant loading, is a topic we treat in detail in several of our STEPn workshops. We have also published some results for physical blends of different latexes (Langmuir, 15, 3250 (1999)).

