soft matter

Photo-tuneable films

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Surfactants are molecules that adsorb at interfaces, thereby modifying surface properties: this is the physical chemistry underlying biological cell membranes, lung action, emulsion and foam formation and detergents. For chemically inert surfactants used in common commercial products, control over molecular aggregation and adsorption states is normally only achieved after significant changes like addition of electrolyte, jumping pH or temperature. The destabilisation or resolution of microemulsions and emulsions is an important process in areas such as pharmaceuticals, organic synthesis, oil recovery, drug delivery, cosmetics and nanotechnology. As such these separations represent possible product recovery/release mechanisms. Small-angle neutron scattering (SANS), coupled with sample contrast variation via selective deuteration, is an especially powerful technique for studying surfactant-containing systems.

A new approach is to use photo-sensitive surfactants, such as compound 1 (figure 1), and now UV light can be used as an external stimulus. In the case of photoscission (photolysis) reactions, oil-loving organic chains can be split away from the water soluble portion (figure 1): Hence with photo-degradable surfactants like 1 it is possible to controllably "switch off" the surface activity, by light-driven generation of inactive compounds like 2 and 3. In fact 3 is actually an oily substance with no interfacial activity whatsoever. The photochemical reactions can be followed, and characterised by Nuclear Magnetic Resonance (NMR) spectroscopy, prior to neutron scattering experiments. Analyses of these NMR spectra suggest that the reaction is essentially complete, and a photo-stationary state is reached after about 110 minutes of irradiation, corresponding to a composition of 37% of 2, 53% of the non-surface active 3 and 10 % residual photo-surfactant 1.

As a good example, consider a water-in-oil nanodroplet dispersion (microemulsion), stabilised by a mixture of 1 and an inert surfactant, which in this case is common Aerosol-OT (figure 2 left). Nanometer-sized spherical water droplets are encapsulated by the interfacial surfactant film, and dispersed in an oily organic solvent (heptane). Application of UV light (hν) is expected to selectively destroy the photo-surfactant 1, leaving the inert co-surfactant Aerosol-OT intact. As a result of the photo-chemical breakdown of 1 the composition of the stabilizing layer will change in favour of the inert surfactant. This should then feed through to changes in the stability of the microemulsion, and also the preferred size of the nanodroplets (figure 2 right).

Figure 3 shows the effect of irradiation with UV light: initially the stable microemulsion sample is transparent (a) since dilute nanometer-sized aqueous droplets are present. After a burst of UV light (b), a milky emulsion containing micron-sized droplets begins to form, which eventually resolves into a clear upper microemulsion phase and a denser, opaque water-surfactant mixture seen at the bottom of the sample (c). Hence UV light has caused a partial destabilisation of the dispersion, through loss of encapsulated water from the organic medium.

Small-angle neutron scattering (SANS), coupled with sample contrast variation via selective deuteration, is the only viable way to study changes of the nanodroplet structure. This is especially powerful since the water droplet cores and interfacial

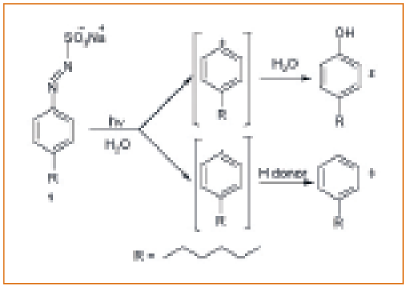

Figure 1: (est expliqué dans le 1er paragraphe du texte).

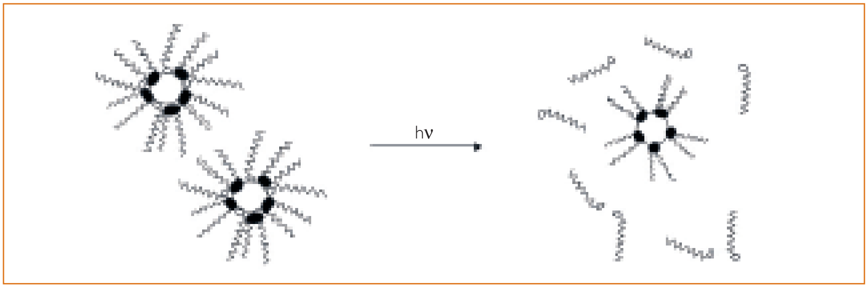

Figure 2: Concept behind photo-tuneable surfaces comprising a photo-destructible surfactant

Figure 3: Shows the effect of irradiation with UV light: initially the stable microemulsion sample is transparent (a) since dilute nanometer-sized aqueous droplets are present. After a burst of UV light (b), a milky emulsion containiing micron-sized droplets begins to form, which eventually resolves into a clear upper microemulsion phase and a denser, opaque water-surfactant mixture seen at the bottom of the sample (c). Hence UV light has caused a partial destabilisation of the dispersion, through loss of encapsulated water from the organic medium.

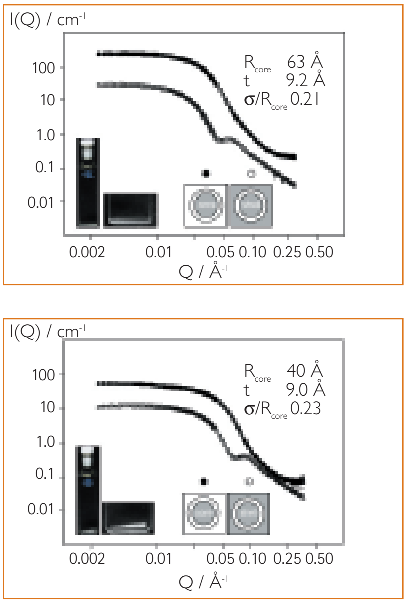

Figure 4: SANS data from water core (●) and surfractant shell (○)contrasts before (a) and after (b) irradiation. Lines are simultaneous fits to both data sets, to find the water droplet radius Rcore, the surface layer thickness t and the polydispersity σ/Rcore.

film can be studied separately in complementary experiments.

The SANS instrument D22 was used to follow this UV-induced shrinkage of the water nanodroplets. In order to obtain detailed information on the effects of irradiation on interfacial and nanodroplet structure, SANS experiments with water core (D_2O + *h*-surfactants + *h*-oil) and surfactant shell contrast (D_2O + *h*-surfactants + *d*-oil) were performed. This latter arrangement highlights a "hollow shell" of surfactant, with a characteristic interference pattern (figure 4). These contrast-variation SANS data were fitted simultaneously. After extensive trials, and based on previous literature, the most appropriate model was found to be for Schultz polydisperse two shell hard spheres. These detailed analyses reveal a shrinkage of the water cores from 63 Å before to 40 Å after UV irradiation, corresponding to a decrease in nanodroplet volume of about 75%. Therefore UV-driven destruction of 1 is equivalent to reducing the effective surfactant concentration, thereby controlling the stability and size of the dispersed water droplets.

Chemicals like 1 represent a new generation of surfactants with added functionality and tuneability, and they offer exciting new possibilities for controlling, surface tensions, molecular aggregation and bulk fluid properties such as visco-elasticity (rheology). Recent research shows this to be a general concept, and photo-surfactants can be employed to control many different properties such as adsorption, micellisation and formation of vesicles, emulsion stability and gelation of both aqueous and organic phases.

M. S.-D. is grateful to the Mexican organisation CONACYT (National Council of Science and Technology, Grant No. 151737) for a scholarship. The work was supported by a grant from the ACORN consortium (EPSRC-DTI).

References: **[1]** Photoresponsive microemulsions, J.Eastoe, M.Sanchez-Dominguez, P.Wyatt, H.Cumber, G.Burnett and R.K.Heenan, Langmuir 19 (2003) 6579
[2] Light-sensitive microemulsions, J.Eastoe, M.Sanchez-Dominguez, P.Wyatt, H.Cumber and R.K.Heenan, Langmuir 20 (2004) 1120