Photo-stabilised microemulsions†

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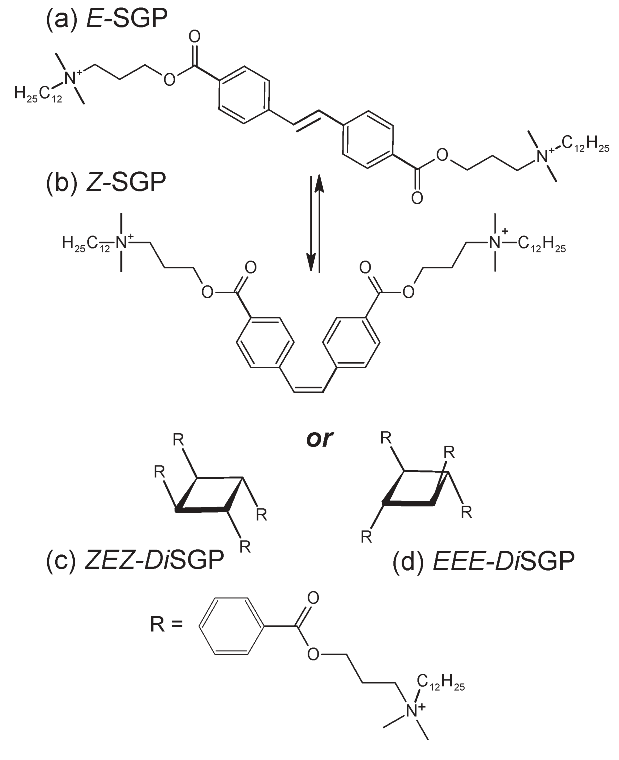
Light-induced stabilisation of water-in-heptane microemulsions has been achieved with a UV-sensitive gemini photo-surfactant.

Recently, synthesis and properties of the photo-sensitive stilbene-containing gemini photo-surfactant (*E*-SGP, Scheme 1) have been reported.[1] In aqueous solutions, UV-induced *E* (*trans*) to *Z* (*cis*) isomerisation of SGP leads to enhanced surface activity, reducing the surface tension by up to $\Delta\gamma = -10$ mN m^{-1}.[1] The purpose of this study was to explore whether such UV-increased surface activity with SGP could also affect properties of oil–water interfaces; specifically to enhance stability of a water-in-oil microemulsion from a mixture that was initially phase separated. This phenomenon could have potential applications in light-induced encapsulation and delivery systems. In these dispersions *E*-SGP was combined with an inert cationic surfactant di-dodecyldimethylammonium bromide (DDAB), a principle that has also been used in aqueous systems.[2] Small-angle neutron scattering (SANS)‡ was used to follow water uptake, which showed that after the action of light an increase in nanodroplet size was accompanied by an increase in volume fraction of dispersed water. Related work with SGP has demonstrated ability to form photo-destructible organogels in toluene (no added water).[3]



Scheme 1 *E*-SGP surfactant (a) and possible photoreactions, (b) *cis*–*trans* isomerization and (c) and (d) dimerization.

Numerous approaches for controlling microemulsion formation and stability have been explored; for example, pervaporation,[4] addition of electrolytes, low or high temperature, pH and saturation with water, *e.g.*[5–7] Since changes in composition and thermodynamic conditions are not always desirable, the use of light presents interesting possibilities. Recently, it has been demonstrated that UV can be used to destabilize microemulsions comprising anionic photo-destructible surfactants, which degrade to yield surface-inactive photo-products.[8,9] Here is reported the first example of the opposite case, with an isomerisable/dimerisable cationic photo-surfactant (Scheme 1), in which a microemulsion is formed after a UV-induced enhancement in surface activity.

Photo-surfactant *E*-SGP was synthesized and characterized as described elsewhere.[1–3] The water-in-oil (w/o) microemulsions were prepared containing d_{16}-heptane (Aldrich, 99.8% D-atom), or h_{16}-heptane (Aldrich, 99.9% HPLC) as appropriate, D_2O (Fluorochem, 99.9% D-atom), DDAB (Aldrich) and *E*-SGP. The composition of these surfactant mixtures may be defined by the mole percentage $X_{SGP} = 100\{[E\text{-SGP}]/([\text{DDAB}] + [E\text{-SGP}])\}$ %. The total concentration of surfactant {[DDAB] + [*E*-SGP]} was constant at 0.10 mol dm^{-3}, and different compositions were investigated with X_{SGP} 0, 2.5, 4.0 and 7.5% and water-to-surfactant ratios w_0 ([water]/[surfactant]) = 25 and 30. Since the initial samples were biphasic (except for $X_{SGP} = 0$, *i.e.* pure DDAB, no SGP), these values represent the water present in the initial separated phases.

Scheme 1 shows possible photoreactions for *E*-SGP (a): *E* (*trans*) to *Z* (*cis*) isomerization (b) and dimerization (c and d). ^{1}H NMR (JEOL Delta/GX270, assignments given in[1]) showed that for a w/o sample with $X_{SGP} = 7.5\%$ and $w_0 = 30$ the post-irradiation photostationary state composition was approximately 81% *Z*-SGP, 15% *E*-SGP and 4% of *ZEZ*-SGP/*EEE*-SGP. Hence, UV generates the more surface active *Z* form in the multi-component mixture. Limitations in the reversibility of the SGP photoreaction, in terms of the formation of a photo-stationary state, have been noted elsewhere.[2]

As shown in the photographs inset to Fig. 1, the irradiated SGP was highly photoactive in microemulsions. Initially, the samples were biphasic, resembling Winsor II systems, with a clear upper microemulsion phase (as indicated by neutron scattering, described below) and a lower cloudy, viscous phase. The appearance of the

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† Electronic supplementary information (ESI) available: details of sample preparation, SANS experiments, and analyses of supporting SANS data. See http://www.rsc.org/suppdata/cc/b5/b503379a/
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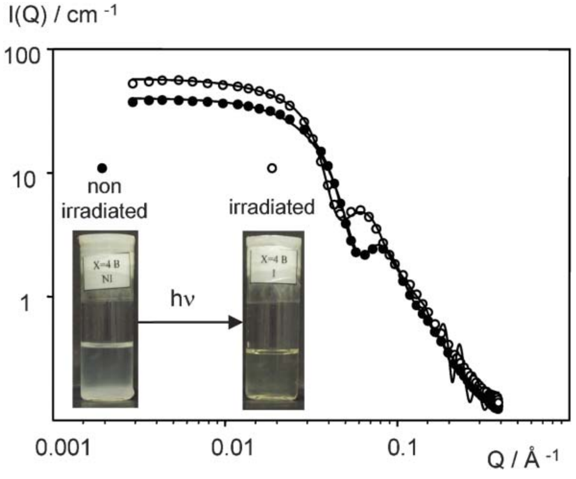

Fig. 1 Changes, before and after irradiation, for water–DDAB–heptane mixtures containing photo-surfactant *E*-SGP at 50 °C. Main figure: small-angle neutron scattering data before (●) and after (○) irradiation for D_2O : H-SGP + H-DDAB : *d*-heptane "shell" contrast microemulsions. Solid lines are fits to the polydisperse core-shell particle model;[10] fitted parameters are given in Table 1. Inset: appearance of samples before (left) and after UV irradiation.

bottom aqueous phase is consistent with the formation of *E*-SGP vesicles in water, which has been documented elsewhere.[1,2]

Shaking, or prolonged sonication of these non-irradiated samples always resulted in phase separation. However, after around 30 minutes of irradiation (supporting material), followed by gentle shaking, clear single phase systems were generated. A control sample with $X_{SGP} = 0$ and $w_0 = 25$ remained unchanged after irradiation; hence the increase in phase stability seen in Fig. 1 may be attributed to the presence of more surface-active *Z*-SGP.

SANS‡ was used to investigate changes in the water droplet and interfacial shell nanostructure, *e.g.*[1–3,8–10] The neutron "shell" contrast employed for the experiments (D_2O : H-surfactants : *d*-heptane) has been used as a sensitive means to highlight structural changes. Scattering from the shell contrast generates maxima and minima, which are characteristic of the inner D_2O nanodroplet radius R_{D_2O} and the interfacial surfactant layer thickness t_{surf}.[10, and references therein.]

Example scattering curves are shown in Fig. 1 for samples with a mole fraction of *E*-SGP $X_{SGP} = 4\%$, $w_0 = 30$ and a total surfactant concentration [SGP + DDAB] = 0.10 mol dm^{-3}. After irradiation the SANS intensity increased considerably, consistent with incorporation of additional D_2O into the microemulsion phase. Table 1 gives parameters fitted to these data sets for a polydisperse spherical core plus shell model:[10] it is clear that the droplet radius and volume fraction of dispersed D_2O (ϕ_{D_2O}) both increase after irradiation, consistent with the enhanced phase stability (Fig. 1 inset).

Table 1 Parameters fitted to SANS data from photo-active microemulsions shown in Fig. 1 using the polydisperse core-shell particle model[10]

	ϕ_{D_2O}	R_{D_2O}/Å	t_{surf}/Å	σ/R_{D_2O}
non-irradiated	0.0347	40.0	14.5	0.24
irradiated	0.0540	53.7	14.5	0.23

[a] Volume fraction of microemulsified water ϕ_{D_2O}; mean radius of water droplet R_{D_2O}; thickness of stabilizing surfactant film t_{surf}; Schulz polydispersity width σ/R_{D_2O}. $T = 50$ °C. Uncertainties: ϕ_{D_2O} ± 10%, R_{D_2O} and t_{surf} ± 2 Å.

The final ϕ_{D_2O} of 0.054 is what would be expected if all the added water were completely dispersed in the microemulsion droplets:[10] this is again consistent with an enhanced surface activity of SGP after UV irradiation. Additional data analyses, for "core" contrast experiments (D_2O : H-surfactants : *h*-heptane) are given in supporting material (Table A), which also indicate increased incorporation of water into the microemulsion after irradiation. The fitted dimensions for R_{DO} and t_{surf} in Tables 1 and A for the post-irradiated samples are consistent with previous SANS studies of microemulsions with DDAB only.[10]

The potential of photo-surfactant *E*-SGP as an active component for controlling microemulsion phase behaviour has been demonstrated. NMR shows that after UV the more surface active *Z*-SGP is predominantly formed, which provides enhanced stabilisation of the oil–water interface, leading to increased incorporation of water into the organic phase, as evidenced by SANS. These results complement previous studies on *E*-SGP,[1,3] illustrating the versatility of this surfactant, both in aqueous and non-aqueous environments, and now at oil–water interfaces. The findings reinforce the importance of molecular design for producing effective and efficient photo-surfactants.

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Notes and references

‡ Small-angle neutron scattering is a diffraction-type technique, normally employing incident beams of $\lambda \sim 1$–10 Å, to reveal structural features (inhomogeneities) on length scales 10–1000 Å. See www.isis.ac.uk/largescale, www.ill.fr and www.chm.bris.ac.uk/pt/eastoe/EastoeHome.htm.

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