Photoinduced Phase Separation

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Here is reported light-induced macroscopic phase separation of aqueous systems, initially containing nanoscopic micellar aggregates. To effect these changes two surfactants are used in combination: a photodestructible anionic (sodium 4-hexylphenyl-azosulfonate C6PAS) and an inert nonionic (hexaethylene glycol monododecyl ether $C_{12}E_6$). NMR and UV–vis spectroscopy have been used to characterize the photochemical breakdown of C6PAS, and small-angle neutron scattering (SANS) has been used to follow decay of the micellar aggregates after exposure to UV light.

A recent review[1] demonstrates the potential of photosurfactants, such as C6PAS, for triggering efficient and irreversible transformations in interfacial and colloidal properties (adsorption, aggregation). Photolysis of this C6PAS[1] switches the hydrophilic surfactant into insoluble hydrophobic photoproducts (hexylbenzene and 4-hexylphenol). The photostationary state composition depends on various factors, including solvent environment and C6PAS concentration; this photochemistry is detailed in Supporting Information.

Phase separation in colloid systems continues to attract interest, owing to potential practical applications in controlled release, delivery, and separation of high-value actives such as pharmaceuticals. Of relevance to this work are salt-induced separations in catanionic surfactant mixtures,[2] surfactant–protein complexes,[3] and membranes.[4] Mixed surfactant systems are studied since enhanced performance can be achieved with blends; thus, commercial applications generally employ mixtures. Anionic–nonionic surfactant mixtures are effective for solubilization enhancement and biodegradation of aromatic hydrocarbons[5–7] and microemulsification of oils.[8] Hence, the factors governing mixed micelle formation have been extensively investigated (e.g., ref 9).

Aqueous mixtures of C6PAS and $C_{12}E_6$ were initially characterized in salt-free solutions as a function of concentration (Supporting Information). Photoirradiation was carried out in quartz cells, with an unfiltered 100 W high-pressure Hg lamp. Photolysis of C6PAS is expected to result in a photogenerated emulsion: as the surfactant breaks down, it feeds the system with oily components (hexylbenzene and 4-hexylphenol), which are emulsified by the remaining inert $C_{12}E_6$. A mixed micelle-to-emulsion transition was confirmed by visual observations and SANS data and analyses (Supporting Information). These emulsions did not resolve, at least over a period of 4 weeks. Next, salting-out electrolyte was added to the systems, thereby reducing the interactions stabilizing the emulsions.

Concentration variation studies indicated that 85 mM total surfactant, with 50:50 C6PAS/$C_{12}E_6$ mixtures in 0.5M NaCl was the most appropriate combination for effecting phase separation. Before irradiation, a transparent yellow (azo phenyl chromophore
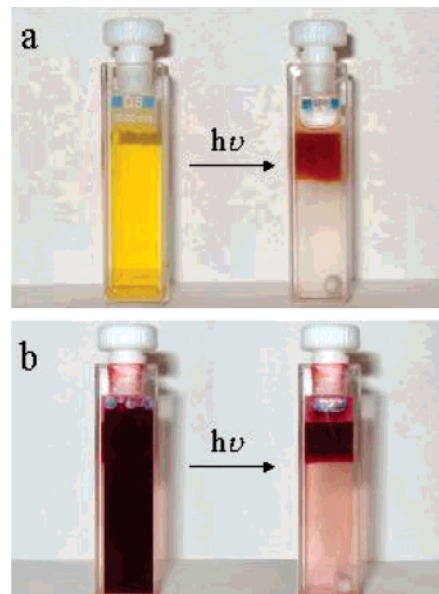
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Figure 1. Phase separation transition after UV irradiation of aqueous 85 mM 50:50 C6PAS/$C_{12}E_6$ mixtures in 0.5 M NaCl (a), now also containing 1.2 mM Nile Red (b).

C6PAS) solution was formed (Figure 1a, left). Incident UV light (exposure time 135 min) resulted in a macroscopic separation of the nascent emulsion into an upper oily layer and a lower aqueous portion (Figure 1a, right). ^{1}H NMR analyses of both phases (Supporting Information) confirmed the composition of the upper oily layer to be dominated by hexylbenzene. In the aqueous lower phase no photodegradation products could be detected by NMR, only trace $C_{12}E_6$ surfactant.

Potential applications of this photoinduced phase separation for light-driven partitioning, or spatial direction, of hydrophobic components were explored by incorporating a water-insoluble dye (1.2 mM Nile Red) into the initial 50:50 C6PAS/$C_{12}E_6$ solutions. Before UV irradiation the solution bears a strong uniform red color, consistent with hydrophobic dye solubilization by micelles (Figure 1b, left). After irradiation, destruction of the initial micelles released the hydrophobic dye, which was seen to partition out of the aqueous phase, and strongly into the coexisting oil-rich portion (Figure 1b, right). Owing to the low concentration ^{1}H NMR could not be used to follow the dye partitioning; thus, UV–vis spectroscopy was used instead (Figure 2). Initial nonirradiated mixtures, with and without dye, were diluted to 21 mM. The absorbance maxima are well resolved (C6PAS $\lambda_{max} \approx 420$ nm, Nile Red $\lambda_{max} \approx 550$ nm). After irradiation, the spectra showed no appreciable absorption from the lower aqueous phase, in the upper oily phase the C6PAS signature was absent, but a strong spectral signal from the dye remained
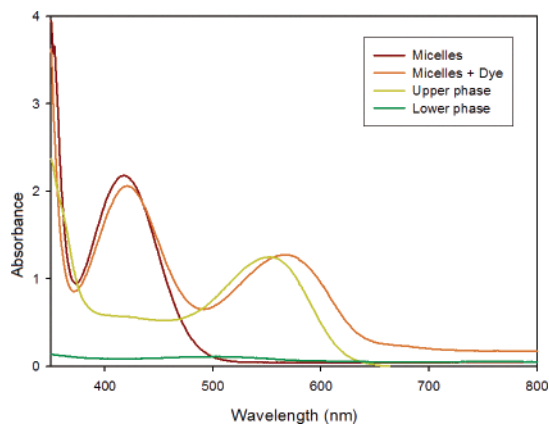
Figure 2. Changes in absorption spectra for 21 mM C6PAS/$C_{12}E_6$ mixtures with and without added Nile Red dye. For post-irradiated systems the upper and lower phases were diluted 256 and 4 times, respectively.

Figure 3. SANS data and fitted functions from D_2O solutions of 85 mM 50:50 C6PAS/$C_{12}E_6$ in 0.5M NaCl, before irradiation (●) and post-irradiated lower phase (○).

(slight blue solvochromatic shift). Assuming approximate Beer—Lambert behavior, the dye partition coefficient K (ratio of apparent concentrations in the oily and aqueous phases) was estimated as ~730.

SANS structural studies of salt-free C6PAS, $C_{12}E_6$ and mixed micelles in D_2O were performed, to follow changes in aggregation with surfactant composition and concentration before and after UV irradiation (Supporting Information). The SANS profile of pure nonionic surfactant micelles displays Q^{-1} scattering and could be fitted by a cylinder form factor (R_1 25 Å, length L 580 Å). SANS data for nonirradiated pure C6PAS micelles display a repulsive $S(Q)$ structure factor peak, characteristic of charged micelles (model fitting, sphere radius R 15 Å, charge 27). Addition of $C_{12}E_6$ to the C6PAS micelles results in depression of the repulsive $S(Q)$, and accompanying intensity increases, consistent with a charged ellipsoid form factor (e.g. for a 50:50 mixture R_1 19 Å, R_2 34 Å, charge 20). Irradiation of the C6PAS/$C_{12}E_6$ mixed micelles caused dramatic increases in SANS intensity (~ 2 orders of magnitude at low $Q \approx 0.008$ Å^{-1}). The changes in SANS intensity before and after UV are consistent with a transition from initially charged ellipsoidal micelles to much larger, noncharged disklike aggregates post-UV (Supporting Information).

Now in 0.5 M NaCl electrolyte prior to irradiation, the electrostatic repulsive $S(Q)$ contribution is effectively screened out (Figure 3), and the SANS profile for the 85 mM 50:50 C6PAS/$C_{12}E_6$ mixture can be fitted by a cylinder form factor only (R_1 18 Å, L 230 Å). The two phases that resolved post-irradiation were split and subjected to separate analysis by SANS. No coherent SANS signal could be resolved from the oily upper phase, suggesting absence of any significant aggregation. Data and analyses for the lower aqueous phase are shown in Figure 3. Compared to the initial micellar solution, the SANS intensity has dropped by approximately 2 orders of magnitude. This indicates a significant reduction in aggregation, in line with the UV—vis and NMR spectra which indicate loss of C6PAS (Figure 2 and Supporting Informa-
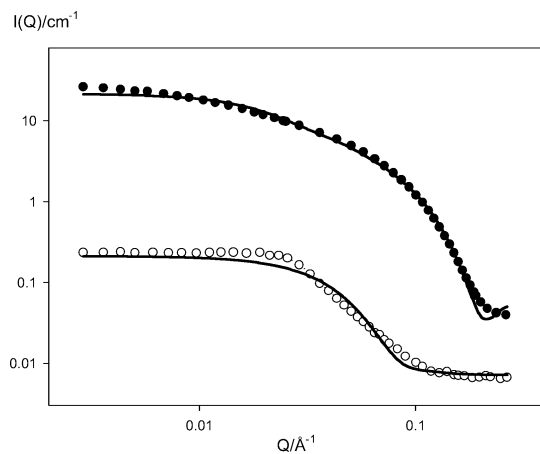
tion). The SANS curve from this lower portion could be adequately fitted as polydisperse spheres with radius R 42 Å, which is consistent with residual surfactant micelles partially swollen with oily photoproducts, contrasted against the D_2O solvent (stabilizing shell of $C_{12}E_6$ molecular length 32 Å, internal oil core radius ~12 Å).

A novel approach of photoinduced phase separation has been demonstrated when a photolabile anionic surfactant is mixed with an inert nonionic surfactant in the presence of salting-out electrolyte. Significant photoinduced changes in aggregation were confirmed by SANS measurements and analyses. The initial mixed micelle systems can disperse an insoluble additive marker dye that may be recovered and spatially segregated from the starting heterogeneous aqueous environment by UV light. This new concept may find applications in light-directed delivery and deposition of hydrophobic and/or hydrophilic constituents of multicomponent functional systems.

Supporting Information Available: Details of photochemistry NMR, UV—vis spectra, SANS data treatment, and analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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