# Photodestructible Vesicles

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## $C_6PAS$ photochemistry

Under UV irradiation akylphenylazosulfonates switch from a hydrophilic (surfactant-based) to a hydrophobic system (photoproducts). As shown in Figure S1, photoirradiation of sodium 4-hexylphenylazosulfonate ($C_6PAS$) yields two different photoproducts. In sufficiently concentrated solutions (above the CMC) both radical and ionic mechanisms occur, yielding respectively the hexylbenzene and the 4-hexylphenol (see refs 19 and 20 in the manuscript).
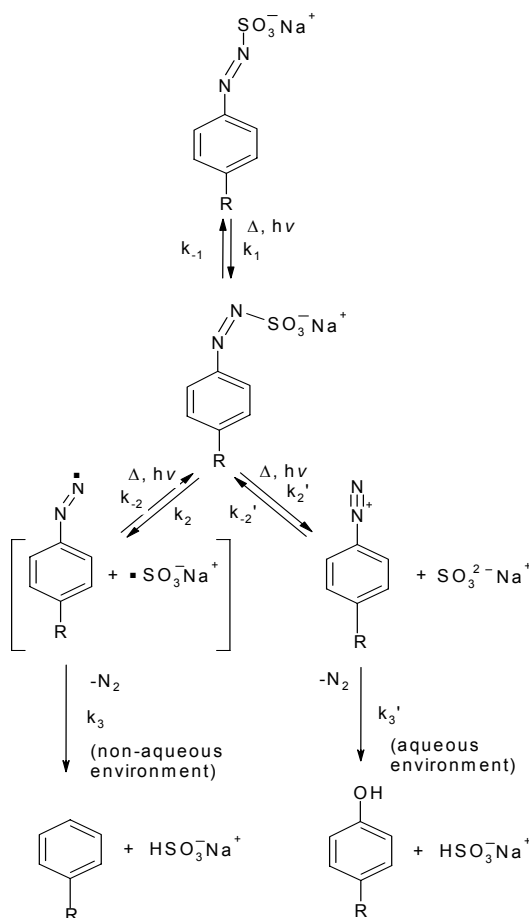


**Figure S1.** Mechanism of photolysis of $C_6PAS$[1] (R=hexyl)

In more concentrated aqueous solutions an insoluble by-product can form, a mechanism for this is proposed by Mezger et al..[2]

$C_6PAS$ shows an intense UV absorption at $\lambda_{max}$=308 nm, responsible for its yellow color. The time of irradiation is based on 270 min for 80 mmol of $C_6PAS$ to allow a complete photolysis. For CTAB alone the same irradiation time was used as for the mixture 1:3 CTAB/$C_6PAS$ at 1.40 wt.%, which corresponds to the highest amount of CTAB introduced. Regarding the changes in spectra of each species alone (Figure S2), it can be assumed that CTAB does not show any absorbance activity (CTAB solutions are colorless) and is not affected by UV light. Photo-irradiation was carried out in quartz cells, with an unfiltered 100W high-pressure white source (Oriel).  At the end of the photo-irradiation, no maximum for $C_6PAS$ is observable in the UV-vis spectrum, meaning the photoreaction is eventually complete. The 1:3 CTAB/$C_6PAS$ mixture at 1.4 wt.% displays exactly the same behavior as for $C_6PAS$ alone. The slight shift in intensity might be due to the milky aspect of the mixture that absorbs less than a pure $C_6PAS$ solution.
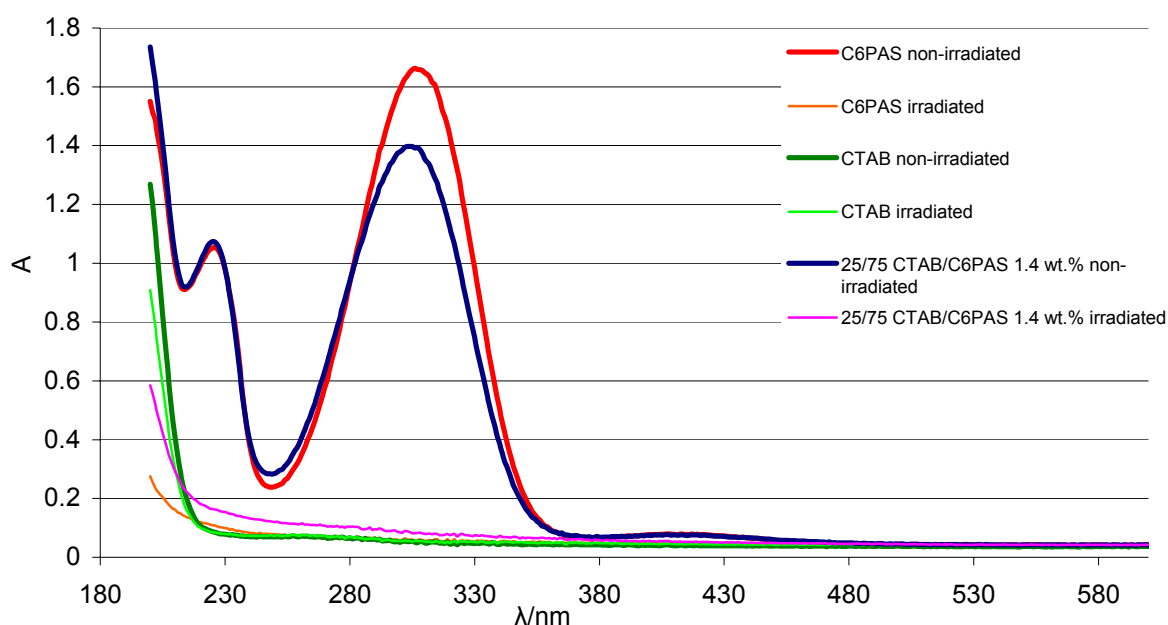


**Figure S2.** Changes in UV-vis absorption spectra of $C_6PAS$ 1.05 wt.% in $D_2O$, of CTAB 0.35 wt.% in $D_2O$, and of the 1:3 CTAB/$C_6PAS$ mixture in $D_2O$ at 1.40 wt.% before and after irradiation

## 1:3 CTAB:C$_6$PAS mixtures

Different concentrations of the catanionic mixture with a ratio 1:3 CTAB/C$_6$PAS in D$_2$O have been investigated. Equilibration of the solutions for one month at 40°C resulted in single-phase, stable, milky systems up to 1.4 wt.%.  All the solutions along this 1:3 molar ratio axis showed the same behavior, before and after UV irradiation, as indicated in Figure S3.
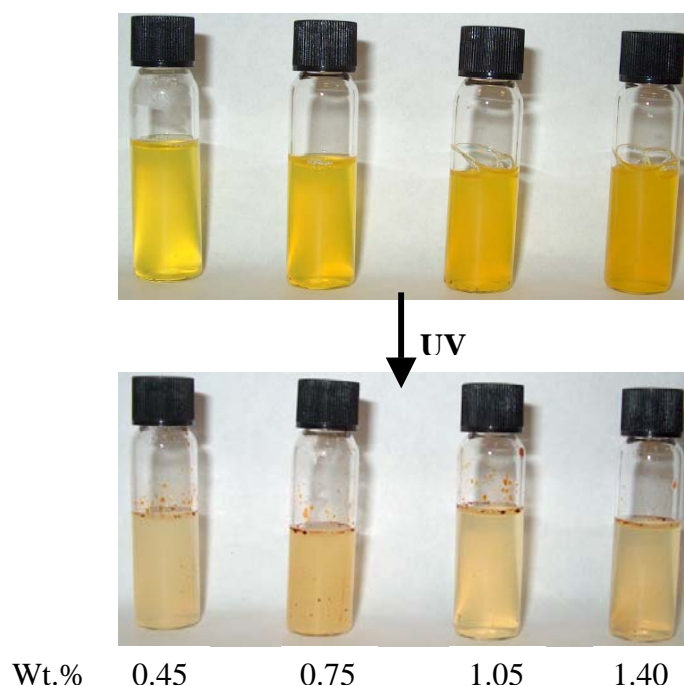


| Wt.% | 0.45 | 0.75 | 1.05 | 1.40 |

**Figure S3.** 1:3 CTAB/C$_6$PAS catanionic mixtures behavior in pre and post-irradiated conditions, with a total concentration up to 1.4 wt.%

## DLS experiments

Measurements were also made for dilution factors of up to 1000, until at the lowest concentration no signal could be detected. As shown by Figure 3 in the manuscript, the measured diameters remain essentially constant for the two systems before and after irradiation, at least for dilutions down to 0.1 wt. %.

**SANS data analysis**

Both of the 1:3 CTAB/$C_6$PAS mixtures before irradiation, for which SANS data are presented in Figure S4, were well described by a Schultz distribution of hollow shell particles (vesicles)[4]. The scattering laws are given in reference 4 (ref 15 of the main manuscript). The post-irradiated samples could be fitted by the model of Kotlarchyck et al.[5] for monodisperse oriented sheets. Reference 4 gives details on the fitting programs used. The difference in scattering length densities ($\Delta\rho$) between $D_2O$ and the surfactants has been calculated using parameters listed in Table S1, and taking in consideration the contribution 1:3 of each surfactant.

As described in the main manuscript, the model reveals the presence of hollow vesicles before irradiation. The theoretical scale factor for this model is proportional to the surfactant volume fraction (Scale=$\Phi*10^{-4}$), and the fitted and estimated values, based on sample compositions, deviated only by a maximum of 6%

## Table S1. Properties of Materials Used

a: at 40°C; b: Calculated from densities

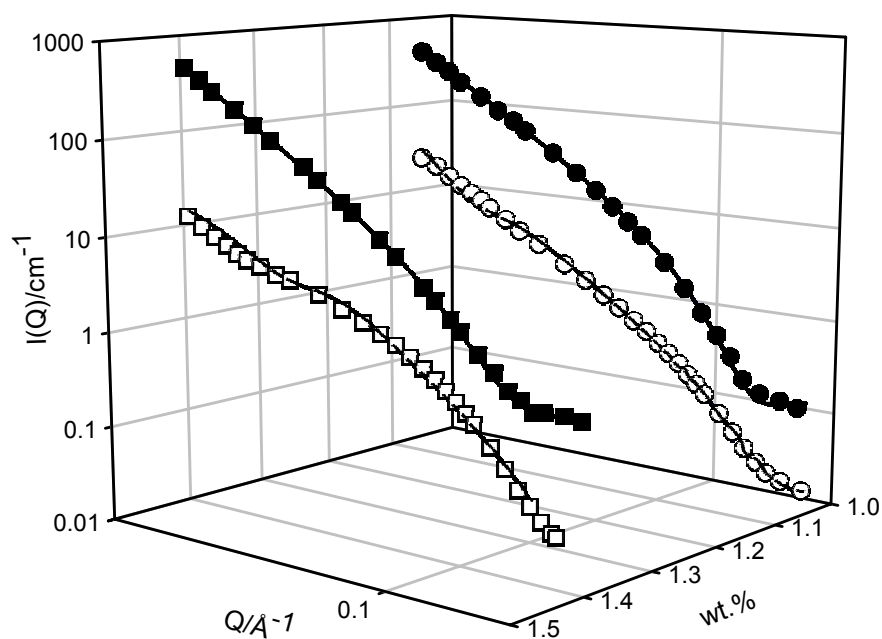| material | density (g.cm$^{-3}$) | volume (Å$^3$) | length[6] (Å) | b[7] (10$^{-12}$ cm) | $\rho$ (10$^{10}$ cm$^{-2}$) |
|---|---|---|---|---|---|
| D$_2$O | 1.1001 [8, a] | 33.2[b] | | 1.915 | 6.400 |
| C$_{16}$H$_{33}$N(CH$_3$)$_3^+$Br$^-$ | | 601.0[6] | 26 | -1.461 | -0.243 |
| C$_{12}$H$_{17}$N$_2$SO$_3^-$Na$^+$ | 0.900 | 539.4[b] | 11 | 5.875 | 1.089 |



**Figure S4.** SANS data and model fits for the 1:3 CTAB:C$_6$PAS mixtures in D$_2$O at 1.05 wt.% (○, before irradiation/● [I(Q)x20], after irradiation) and 1.40 wt.% (□, before irradiation/■ [I(Q)x50], after irradiation)

## References

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