

A Photodestructible Surfactant

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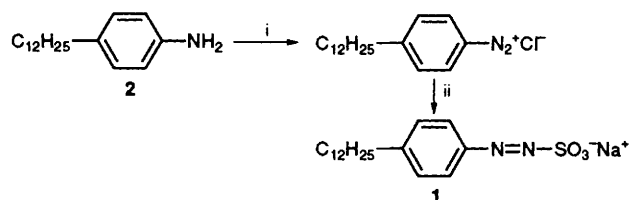
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The azo-containing surfactant sodium 4-dodecylphenylazosulfonate has been shown to exhibit surface activity which can be destroyed by irradiation with ultraviolet light.

As part of a wider research programme aimed at developing organic materials whose hydrophobicity–hydrophilicity balance can be switched by photo-irradiation, we now report on a photo-destructible surfactant. So-called destructible surfactants which are cleaved by acid¹ or base² hydrolysis are well known, however less well known are those which are cleaved thermally³ or photolytically⁴ or which undergo addition⁵ or redox reactions⁶ to destroy their amphiphilic properties. The only previous example of a photochemically destructible surfactant was produced *via* an eight-step synthesis, and the molecule did not contain a labile linkage which could be easily monitored. We now report on a thermally stable azo-containing destructible surfactant which can be produced in a two-step, one-pot reaction and whose decomposition can be followed conveniently by ultraviolet/visible spectroscopy.

Sodium 4-dodecylphenylazosulfonate **1** was synthesised from 4-dodecylaniline **2** by the adaption of previous chemistry⁷ (Scheme 1). The readily available 4-dodecylaniline **2** was diazotised under standard conditions, the acidic solution was neutralised with sodium acetate and subsequent coupling with sodium sulfite gave the azosulfonate **1**.[†]

The surface active properties of **1** were confirmed by the foaming of its aqueous solutions and from its ability to micellise in water. Its critical micelle concentration (CMC) was determined from equilibrium air–water surface tension data using a Du Noüy tensiometer⁸ (platinum ring method) and was found to be $6.02 \times 10^{-4} \text{ mol dm}^{-3}$ (Fig. 1).



Scheme 1 Reagents and conditions: i, NaNO_2 , $3 \text{ mol dm}^{-3} \text{ HCl}$, 0°C ; ii, NaOAc , Na_2SO_3 , 0°C , 16%

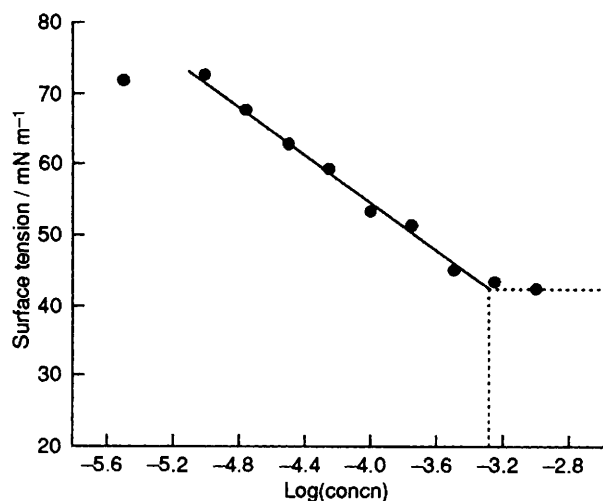


Fig. 1 Plot of surface tension at various concentrations of **1** in water at 25°C . The dotted lines indicate the critical micelle concentration ($6.02 \times 10^{-4} \text{ mol dm}^{-3}$).

In addition **1** was also able to solubilise the oil-soluble dye, Waxoline Red, in aqueous solutions, presumably by incorporation of the latter in the interior of micelles.

The photoactivity of **1** was demonstrated by irradiation of aqueous solutions of **1** with ultraviolet light.[‡] The change in surface tension of the solutions is shown in Fig. 2, where we interpret the rise in the surface tension to the value close to that of water (72 mN m^{-1}) as unambiguous evidence for the destruction of **1**. A solution of **1** ($1.0 \times 10^{-3} \text{ mol dm}^{-3}$) which had Waxoline Red dye incorporated within its micelles yielded an isotropic red coloured solution. On photolysis the solution became colourless. We believe photolysis destroys the micelles and the tiny quantity of dye present phase separates. Photo-destruction of **1** is confirmed by the ultraviolet/visible spectra of solutions before and after irradiation, where the loss of the band due to the azo group is clearly demonstrated (Fig. 3).

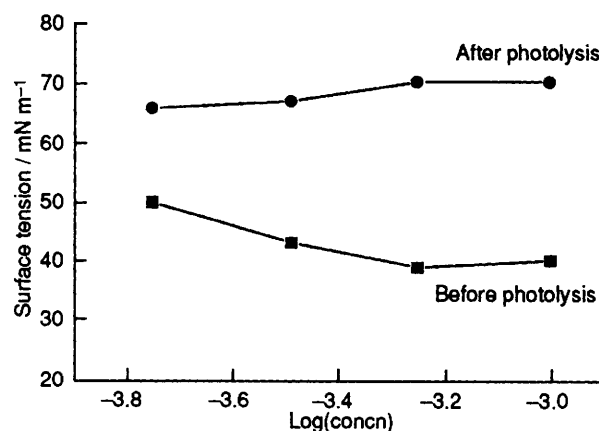


Fig. 2 Plot of surface tension at various concentrations of **1** in water at 25°C , before and after photolysis. The data come from four separate experiments; in each case the solutions were photolysed for 15–20 h with an unfiltered high-pressure Hg arc.

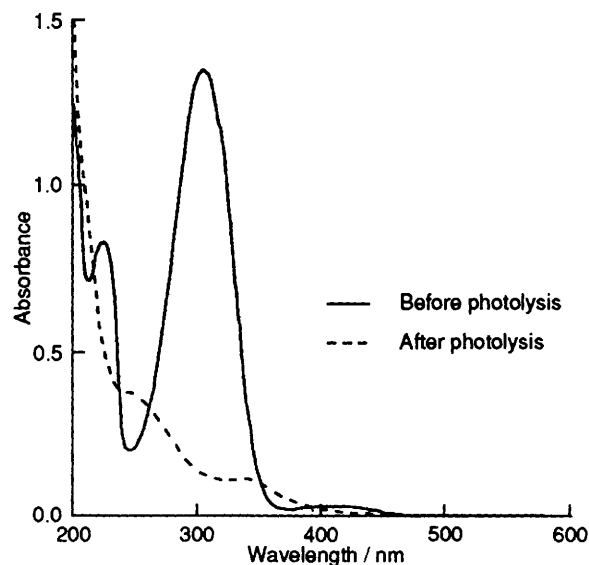


Fig. 3 UV-VIS absorption spectra of **1** in water ($1.0 \times 10^{-4} \text{ mol dm}^{-3}$), before and after photolysis (40 min unfiltered high-pressure Hg arc)

We believe that molecules similar to **1** offer considerable opportunities in the field of water-borne coatings (*e.g.* paints) where an efficient switch from a water-based (hydrophilic) delivery system to a water-resistant (hydrophobic) final film is essential for high performance. This switch from hydrophilic to hydrophobic properties is currently only achievable inefficiently *via* thermal loss of NH₃ from ammonium carboxylate residues.⁹ Incorporation of oil-soluble dyes into micellar solutions of **1** also provides a potential route to a novel pseudo photobleaching technology.

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Footnotes

† C, H, N and S analysis and spectroscopic data are in agreement with the structure.

‡ All photolyses were carried out in a Rayonet R.P.R-208 Photochemical Reactor fitted with RUL-3000 Å lamps.

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