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Synthesis, characterization and applications of azo-containing photodestructible surfactants

Ian R. Dunkin,* Andreas Gittinger, David C. Sherrington and Paul Whittaker

University of Strathclyde, Department of Pure and Applied Chemistry, Thomas Graham Building, 295 Cathedral Street, Glasgow, G1 1XL UK

Photodestructible surfactants, sodium 4-(2-cyano-2-undecylazo)benzoate and a series of sodium 4-alkylphenylazosulfonates, have been synthesized and were shown to be surface active in solution, each exhibiting a distinct critical micelle concentration (CMC). UV irradiation of aqueous solutions of the alkylazobenzoate led to a distinct increase in surface tension, but even after complete photolysis significant surface activity remained, indicating a substantial amount of cage recombination after nitrogen evolution. UV irradiation of sodium 4-dodecylazosulfonate caused a photoscission reaction, completely destroying its surface active properties. In the case of azosulfonates with shorter alkyl chains, however, some residual surface activity remained after complete removal of the azo linkage, indicating that secondary surfactants were formed by the photolysis. The 4-alkylphenylazosulfonates were able to solubilize an oil-soluble dye in water to produce isotropic coloured solutions. Photoirradiation of these solutions led to complete loss of colour, presumably as a result of microprecipitation of the dye. The azosulfonate surfactants also readily emulsified vinyl monomers, such as styrene, in water. Attempts to achieve emulsion polymerization led to only low conversion of monomer, most likely owing to side reactions between initiating radicals and the azo linkage of the surfactant, leading in turn to disruption of the micelle.

Introduction

The self organization of amphiphiles into ordered assemblies such as micelles, bilayers or vesicles is based on the existence of both hydrophilic and hydrophobic moieties in one molecule. The removal of one of these moieties from the amphiphile by a scission reaction or the alteration of the balance between hydrophilicity and hydrophobicity will cause a disruption of the organized assembly.

The most common type of assembly destabilization occurs through cleavage of the hydrophobic and hydrophilic portions of the amphiphile (headgroup cleavage). So called 'destructible surfactants' based on headgroup cleavage by acid hydrolysis,[1] base hydrolysis,[2] and thermolysis[3] are known. Destabilization of the organized architecture by disruption of the surfactants' hydrophilic–hydrophobic balance has also been achieved by redox[4] and Diels–Alder reactions[5] and by polymerization.[6]

Photochemistry has also been utilized to cause the disruption of amphiphiles. There are several classes of photoreaction which can produce such a disruption, and these can be loosely classed as: (*i*) photoinduced *cis–trans* isomerizations, (*ii*) photoinduced polarity changes, (*iii*) photoscission of links between hydrophilic headgroups and hydrophobic tails.

With the first of these classes, irradiation of a chromophore within the hydrophobic part of the molecule leads to a change in the packing of the assembly. It is not known, as a general rule, whether the free energy of micellization for *cis* and *trans* isomers can be expected to be distinctly different, but examples of changes in the state of aggregation in bilayer membranes derived from single chain amphiphiles containing azo-benzene moieties have been observed.[7]

Photoinduced polarity changes can involve changes in the hydrophilicity of the headgroup, brought about by photoisomerization, or more modest polarity changes in the photosensitive chromophore. As examples, Ringsdorf has investigated the conversion of both single and double chain photosensitive mesoionic 1-iminopyridinium ylides to 1,2-diazepines,[8] while surfactant spiropyrans have been investigated by a few groups.[7b,9]

Of greatest relevance to the work described in this paper are reactions of the third class: photoscissions of links between the headgroups and tails of surfactant molecules. To be useful the photolabile group should be reasonably stable under the heat and light of normal working conditions. Additionally, the intermediate species produced on photolysis should not be long lived and should undergo an almost quantitative cleavage in a known decomposition pathway with no rearrangement to side-products. Subsequently, the polar headgroup should remain solubilized while the hydrophobic tail should precipitate.

Several research groups have investigated the Norrish Type II cleavage of ketones as potential photoscission reactions for cationic and anionic headgroups,[10] but only one group managed to avoid concomitant cyclization of the intermediate biradical. In contrast Japanese workers have successfully utilized the photochemical cleavage of the C–P bonds of *para*-substituted benzylphosphonic acids[11] or (*para*-substituted pyridinomethyl)phosphonates[12] in the design and synthesis of photocleavable surfactants.

A double chain, light-sensitive amphiphile based on a substituted quaternary ammmonium salt has also been shown to undergo photolytic headgroup cleavage,[8b,c] while a similar cleavage has been achieved from a double chain, light-sensitive benzenediazonium salt.[13]

The synthesis of micelle-forming photocleavable surfactants with an azo-linkage as the photolabile group, joining an anionic hydrophilic group to a hydrophobic hydrocarbon tail has recently been reported by ourselves[14] and others.[15] This paper provides a full account of our results with sodium 4-alkylphenylazosulfonates and an anionic azonitrile surfactant.

We believe that photocleavable surfactants have considerable potential 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 achievable only inefficiently *via* thermal loss of NH_3 from ammonium carboxylate residues.[16] Incorporation of oil-soluble dyes into micellar solutions containing photocleavable surfactants also provides

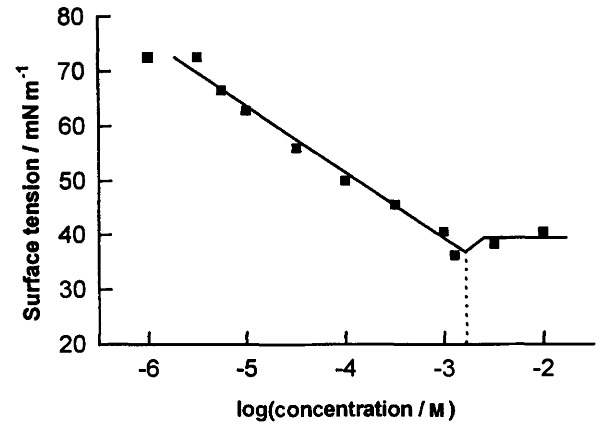


Fig. 1 Plot of surface tension as a function of the logarithm of concentration for **4** in water at 25 °C

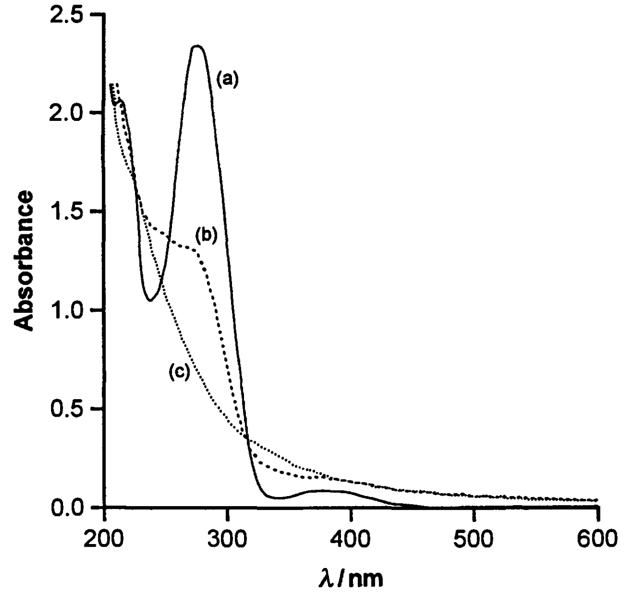


Fig. 2 UV–VIS absorption spectra of **4** in water (3.2×10^{-4} mol dm^{-3}): (*a*) before photolysis, (*b*) after 2 h photolysis, (*c*) after 21 h photolysis

scope for development of novel pseudo-photobleaching technology.

Results and discussion

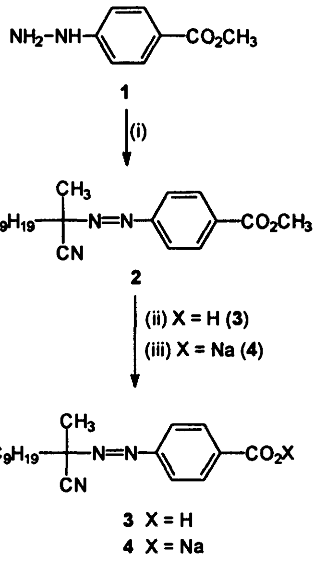
A cyanodecylazobenzoate surfactant

Initial attempts to produce a surfactant containing a photolabile azo linkage centred on mixed aromatic–aliphatic azonitriles. The aromatic azonitrile surfactant **4** was produced according to Scheme 1. The hydrazine formed in the initial reaction from methyl 4-hydrazinobenzoate **1**, undecan-2-one and sodium cyanide was not isolated, but oxidized immediately with sodium hypochlorite to give the azonitrile ester **2**. This ester was conveniently converted into the acid **3** or the sodium salt **4** by hydrolysis using conditions previously reported for the hydrolysis of esters in the presence of azonitriles.[17]

The sodium salt **4** was found to be distinctly surface active. The CMC was determined from equilibrium air-water surface tension data obtained with a Du Noüy tensiometer (platinum ring method) and found to be 1.57×10^{-3} M (Fig. 1). The salt **4** could be destroyed photochemically. The UV–VIS spectra in Fig. 2 clearly show the removal of the absorption at 278 nm, attributable to the azo group, as the photolysis proceeded. Surface tension measurements of solutions of **4** after photolysis showed that the surface tension increased, though the increases were small (post-irradiation surface tensions: 48 mN m^{-1} at 1.0×10^{-3} M, and 44 mN m^{-1} at 6.31×10^{-3} M). These increases in surface tension, even though all the azo linkages had been cleaved, suggest that there was a significant amount of cage recombination of the radicals after evolution of nitrogen. This is not an unreasonable suggestion as it has been shown for azoisobutyronitrile (AIBN) that the cage effect operates at about 40%.[18]

Table 1 Critical micelle concentrations (CMC) of sodium 4-alkylphenylazosulfonates determined from surface tension measurements

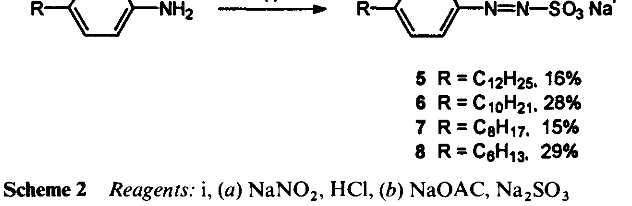
Surfactant	CMC/M
5	6.02×10^{-4}
6	1.43×10^{-4}
7	1.08×10^{-3}
8	1.31×10^{-2}



Scheme 1 *Reagents:* i, undecan-2-one, NaCN, toluene-*p*-sulfonic acid, then NaOCl, 14%; ii, 50% NaOH in MeOH, then HCl, 89%; iii, 50% NaOH in MeOH, 92%

Azosulfonates

Synthesis. The sodium 4-alkylphenylazosulfonates **5–8** were synthesized from the corresponding substituted anilines by the adaption of established chemistry.[19] The anilines were each diazotized under standard conditions, and the resulting diazonium salts treated with sodium sulfite to give the azosulfonate (Scheme 2).



Scheme 2 *Reagents:* i, (*a*) NaNO$_2$, HCl, (*b*) NaOAC, Na$_2$SO$_3$

Surface active properties of azosulfonates. The azosulfonates **5–8** were all surface active, as confirmed by the observed foaming of their aqueous solutions and their ability to micellize in water. CMCs were determined for all the azosulfonates. The corresponding plots of surface tension *vs.* log (concentration) are shown in Figs. 3–6, each of which indicates a definitive CMC. The data for all four surfactants are collated in Table 1, where the CMC values can be clearly seen to increase as the chain length decreases.

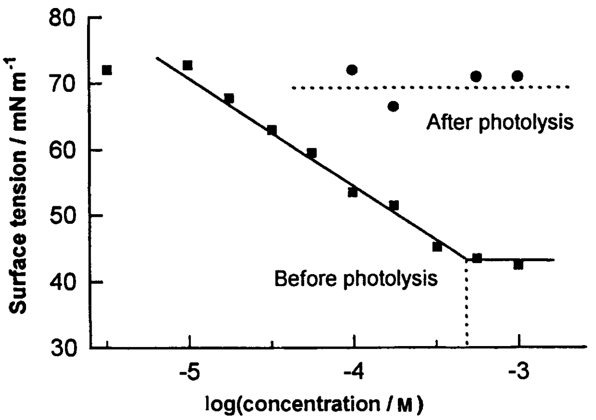


Fig. 3 Plot of surface tension as a function of the logarithm of concentration for **5** in water at 25 °C

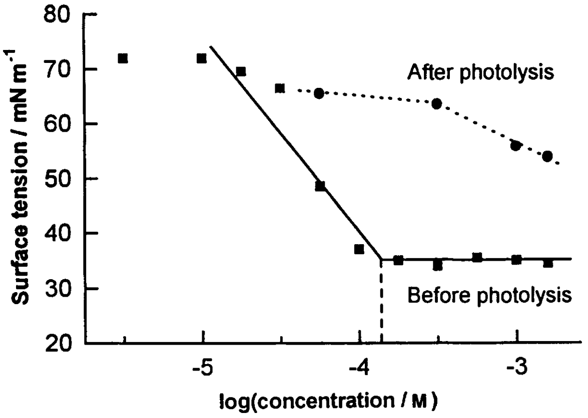


Fig. 4 Plot of surface tension as a function of the logarithm of concentration for **6** in water at 25 °C

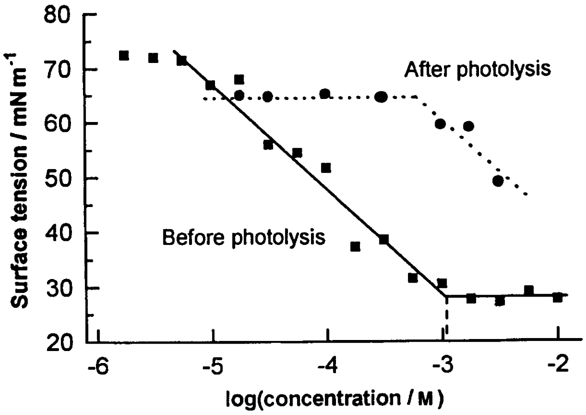


Fig. 5 Plot of surface tension as a function of the logarithm of concentration for **7** in water at 25 °C

Removal of surface active properties of azosulfonates. In order to demonstrate the destruction of micelles of the azosulfonates by irradiation with UV light, values for the surface tension of aqueous solutions of the azosulfonates were measured following photolysis (Figs. 3–6). The rise in the surface tension of solutions of **5** to values close to that of water (72 mN m^{-1}) shown in Fig. 3 is interpreted as unambiguous evidence for the photodestruction of **5**. The changes in surface tension for the other surfactants (**6**, **7** and **8**) shown in Figs. 4–6, however, were less pronounced, and the degree of change seemed to decrease as the alkyl chain length decreased. The surface tension of photolysed solutions of **8** did not approach that of water; instead it appeared that a new curve was observed due to the photoproducts present in the mixture, suggesting that the photoscission produced a new surfactant—probably the corresponding alkylphenol as its sodium salt (see below)—with a very different CMC. The possibility that the photolysis did not proceed to completion and that the residual surface activity of the solutions can be attributed to unphotolysed surfactant can be discounted by analysis of the UV–VIS spectra of **8** (which exhibited the lowest increase in surface tension), where the total removal of the absorption due to the azo group is clearly demonstrated (Fig. 7).

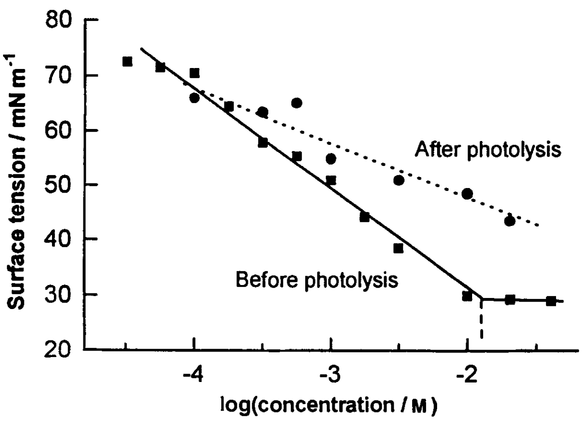
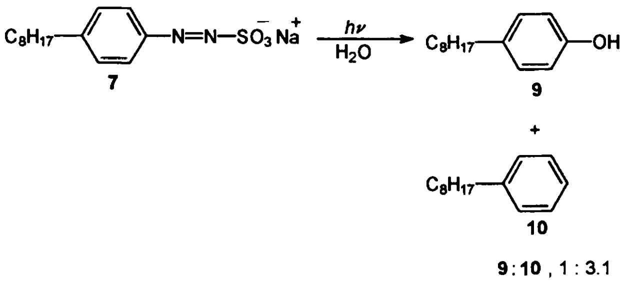


Fig. 6 Plot of surface tension as a function of the logarithm of concentration for **8** in water at 25 °C

The possibility of a new surfactant being produced by the photodecomposition of the sodium 4-alkylphenylazosulfonates was investigated by photolysing compound **7** on a large scale and identifying the photoproducts. The choice of **7** for this study was made because the potential photoproducts needed for comparison, 4-octylphenol **9** and 1-phenyloctane **10**, are readily obtainable commercially. Azosulfonate **7** was photolysed until no starting material remained. Work-up, followed by GC analysis, showed that both the phenol **9** and the hydrocarbon **10** were present, with the hydrocarbon being the major constituent (Scheme 3).



Scheme 3

The excess of hydrocarbon over the phenol is at odds with previous photolyses of diazonium salts reported in the literature. Photolysis of nitrobenzenediazonium salts in water failed to produce any of the corresponding nitrobenzenes.[20] This was interpreted as evidence for the decomposition proceeding by an ionic mechanism. In ethanol, however, the major products were nitrobenzenes, indicative of a radical mechanism. The products of the photolysis observed in our experiments, **9** and **10**, are easily explained if a radical mechanism and an ionic mechanism occur in competition (Scheme 4). It is possible that the ionic mechanism occurs for surfactant dissolved in the bulk aqueous phase, while the radical mechanism occurs for surfactant molecules in the more hydrophobic micelle.

Wokaun and co-workers have also found large amounts of hydrocarbon products from the photolyses of various azo-containing compounds, when the photolyses were carried out in micellar environments.[21] Similarly, when the photolysis of a lipid derived from a substituted benzylammonium salt was

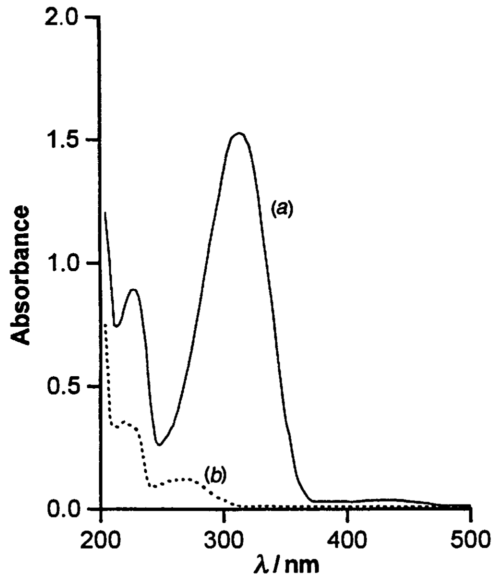
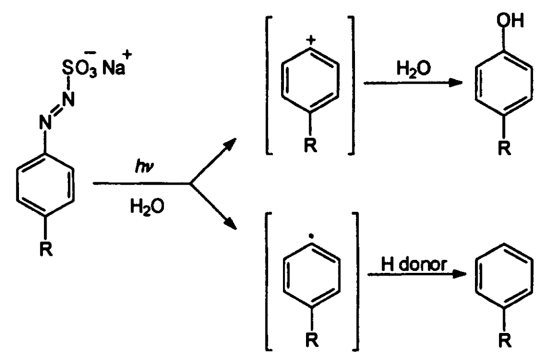


Fig. 7 UV–VIS absorption spectra of **8** in water (1.0 × 10^4 mol dm^{-3}): (*a*) before photolysis, (*b*) after 22 h photolysis



Scheme 4

carried out in a liposome, the observed photoproduct was the toluene derivative.[8b,c] The water solubility of the phenol **9** is extremely low (*ca.* 1 mg in 50 ml), hence the residual surface activity after photolysis is unlikely to be due to **9** but much more likely due to its sodium salt.

To demonstrate further the destruction of azosulfonate micelles by photolysis, an oil-soluble (aqueous insoluble) dye, Waxoline Red, was shaken with solutions of the azosulfonates at concentrations above their CMCs to produce isotropic red solutions. This showed that the dye was included within the interiors of the micelles. On photolysis, the bright red solutions became essentially colourless, presumably as a result of microprecipitation of the water-insoluble dye as micelles were destroyed. This was quantified by comparing absorbance measurements at 510 nm (λ_{max} of Waxoline Red) for solutions of azosulfonates above their CMCs, (*i*) without dye incorporation, (*ii*) with dye incorporation, and (*iii*) with dye incorporation and photolysis (Table 2). The results clearly show the destruction of the azosulfonate micelles. Furthermore, the precipitation of the dye indicates that any secondary surfactant produced by photolysis is well below its CMC, even at relatively high concentrations of the initial surfactant.

Emulsion polymerization with the azofulfonates. Emulsion polymerizations of both styrene and methyl methacrylate were attempted, using the synthesized azosulfonates as emulsifiers. The attempted polymerizations used a variety of surfactant concentrations (various mol% based on monomer) related to the water solubility of each surfactant. The reactions were initiated in various ways: thermally, with potassium persulfate or azoisobutyronitrile, and by redox initiation using *N*,*N*,*N*′,*N*′-tetramethylethylenediamine and ammonium persulfate (Table 3).

In all cases with the azosulfonates, the emulsion polymerizations failed, with the emulsion collapsing and the polymerization not proceeding to completion. In all cases monomer remained unpolymerized. A possible cause of collapse of the emulsion could be the attack of initiator radicals on the azo-linkage of the emulsifier, which would alter the lipophilic balance of the surfactant thus leading to micelle collapse. Aromatic azosulfonates have been shown previously to act as radical traps.[22]

Experimental

General

Melting points were determined on a Gallenkamp apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 397 spectrometer, and UV–VIS spectra on a Pye-Unicam SP 800. NMR spectra were recorded on a Bruker WM 250 instrument, using $SiMe_4$ as the internal standard throughout. Microanalyses were performed on a Perkin-Elmer 2400 analyser, and MS were recorded on an AEI MS9 mass spectrometer.

Materials

All materials used were commercial samples, with the exception of Waxoline Red dye, which was supplied by ICI. Before use, liquid amines and undecan-2-one were distilled; methyl methacrylate and styrene were washed with aq. NaOH and water, dried and then distilled at reduced pressure under nitrogen; all chromatographic solvents were distilled, while other solvents were purified by standard methods. Otherwise materials were used as received. In the following procedures, petrol refers to light petroleum (boiling range 40–60 °C) and ether refers to diethyl ether.

Photolyses

All photolyses were carried out in a Rayonet RPR-208 Photochemical Reactor fitted with RUL-3000 Å (300 nm) lamps, using reaction vessels of various sizes. The unbuffered aqueous solutions were stirred internally. Photolysis times varied depending on solution concentrations.

Surface tension measurements

All surface tensions were measured with a Du Noüy platinum ring tensiometer supplied by White Electrical Instruments Co. Ltd. Surfactant solutions were prepared in doubly distilled water, and full details of our methodology have been decribed previously.[23] Surface tension measurements after photolysis were obtained after the solutions had been filtered through 0.45 µm cellulose nitrate membrane filters.

Gas chromatography

GC was performed on a Perkin-Elmer F33 instrument fitted with a flame ionization detector. The glass column used was two metres long and the packing was 2.5% silicon gum rubber E 301 on Chromasorb G. Products were identified by comparison with authentic samples and product yields were determined using the internal standard method.

Dye experiments

The surfactant solution, at a known concentration above its CMC value, was shaken with Waxoline Red dye for 1 h and the solution left to equilibrate overnight. The solution was filtered through a paper filter to remove excess dye, and the UV–VIS spectrum of the filtrate recorded. The solution was photolysed and the UV–VIS spectrum recorded again. In some cases with a high concentration of surfactant (*e.g.* 0.02 M of **8**), the solution was filtered through a 0.45 µm cellulose nitrate membrane filter to remove particulate material before re-recording the UV–VIS spectrum. As a check, it was ascertained that a solution incorporating the red dye could be passed through this filter without removal of the dye from the solution.

Table 2 Measured absorbances at 510 nm, before and after UV photolysis, for surfactant solutions of the azosulfonates **5**–**8** containing Waxoline Red, and comparison with surfactant solutions containing no dye

Surfactant	Conc./M	Before photolysis	After photolysis	No dye
5	1.00×10^{-3}	0.39	0.03	0.02
6	1.58×10^{-3}	0.36	0.00	0.05
7	5.64×10^{-3}	0.43	0.00	0.08
8	0.02	1.10	0.00	0.30

Table 3 Attempted emulsion polymerizations of azosulfonates

Run	Surfactant	Monomer	Initiator[a]	T/°C	Outcome
1	**5** (0.5%)	Styrene	$K_2S_2O_8$ (2.0%)	60	Emulsion collapsed, clear soln.[b]
2	**5** (0.5%)	Styrene	$K_2S_2O_8$ (2.0%)	80	Emulsion collapsed, red oil on surface of soln.
3	**6** (5.0%)	Styrene	$K_2S_2O_8$ (2.0%)	60	Emulsion collapsed, red oil on surface of soln.
4	**6** (2.0%)	MMA[c]	TMEDA[d] (2.0%) $(NH_4)_2S_2O_8$ (2.0%)	Room temp.	Emulsion collapsed, polymer coagulated
5	**8** (2.1%)	MMA	$K_2S_2O_8$ (2.0%)	80	Emulsion separated out
6	**8** (2.1%)	MMA	AIBN (2.0%)	80	Polymer coagulated, incomplete polymerizn.
7	**8** (4.2%)	MMA	AIBN (3.0%)	80	Polymer coagulated, incomplete polymerizn.
8	**8** (2.1%)	MMA	TMEDA (2.0%) $(NH_4)_2S_2O_8$ (2.0%)	Room temp.	Incomplete polymerization

[a] Percentages of surfactant and initiators are mol % based on the monomer. [b] In contrast to a report of a successful polymerization of MMA under similar conditions [ref. 15(*d*)]. [c] MMA = methyl methacrylate. [d] TMEDA = tetramethylethylenediamine.

Syntheses

Methyl 4-hydrazinobenzoate **1**. This compound was synthesized according to a previous method.[24]

Methyl 4-(2-cyanoundecan-2-ylazo)benzoate 2

To a stirred solution of methyl 4-hydrazinobenzoate **1** (3.32 g, 0.02 mol) in methanol (90 ml), undecan-2-one (3.40 g, 0.02 mol) was added followed by *p*-toluenesulfonic acid (5.71 g, 0.03 mol) and sodium cyanide (1.48 g, 0.03 mol), and the mixture was stirred for 120 h. The methanol was removed under reduced pressure and the mixture partitioned between water and dichloromethane. The organic layer was washed with water, dried (Na_2SO_4) and evaporated under reduced pressure. The residue was dissolved in methanol (100 ml), cooled to 0 °C and oxidized with sodium hypochlorite by dropwise addition over 3 h followed by warming to ambient temperature over 16 h. The resulting mixture was extracted into dichloromethane, washed with water, dried (Na_2SO_4) and evaporated under reduced pressure, and the residue triply chromatographed on silica gel using petrol–chloroform mixtures to give **2** as an orange oil (0.99 g, 14%) (Found: C, 69.4; H, 8.7. $C_{20}H_{29}N_3O_2$ requires C, 69.9; H, 8.5%); ν_{max}/cm^{-1} 2924s, 2854s, 2245w, 1736s, 1607m, 1478m, 1445m, 1413m, 1380w, 1283s, 1193w, 1122m, 1014m, 971w, 874m, 777m and 701m; $\delta_H(CDCl_3)$ 0.86 (3 H, t, J 6.5, CH_2CH_3), 1.16–1.43 (12 H, m, 6 × CH_2), 1.43–1.61 (2 H, m, CH_2), 1.77 (3 H, s, C-CH_3), 2.00–2.18 (2 H, m, CH_2), 3.95 (3 H, s, CO_2CH_3) and 7.78, 8.16 (4 H, dd, 1,4-disub. benzene ring); $\delta_C(CDCl_3)$ 14.23 (CH_2CH_3) 22.80, 24.58, 29.37, 29.42, 29.51, 29.57, 31.98, 38.87 (8 × CH_2), 24.35 (C-CH_3), 52.57 (CO_2CH_3), 73.33 (C-CN), 119.44 (CN), 122.83, 130.80 (CH aromatic), 132.80, 153.44 (C aromatic), 166.36 (CO_2-CH_3); *m/z* 135.0437 [100.0, M – $C_9H_{19}C(CH_3)(CN)N_2$], 163.0512 [82.9, M – $C_9H_{19}C(CH_3)CN$], 180.1759 (1.0, M – $N_2C_6H_4CO_2CH_3$).

4-(2-Cyanoundecan-2-ylazo)benzoic acid 3

The ester **2** (176 mg, 0.51 mmol) was stirred with a 50% sodium hydroxide solution (2.1 mmol) in methanol (10 ml) for 48 h. After dilution with water the mixture was acidified with dilute hydrochloric acid and extracted with chloroform, dried (Na_2SO_4) and evaporated under reduced pressure. Recrystallization of the residue from petrol gave **3** as a yellow powder (151 mg, 89%), mp 112–114 °C (Found: C, 69.0, H, 8.3. $C_{19}H_{27}N_3O_2$ requires C, 69.3; H, 8.3%); ν_{max}/cm^{-1} 3062w, 2934m, 2921s, 2857s, 2238w, 1686s, 1615w, 1472w, 1431m, 1308m, 1298m, 1125w, 1012w, 951w, 880m, 777m, 726w and 696w; $\delta_H[(CD_3)_2SO]$ 0.79 (3 H, t, J 6, CH_2CH_3), 1.10–1.45 (14 H, m, 7 × CH_2), 1.73 (3 H, s, CH_3), 2.03–2.19 (2 H, m, CH_2) and 7.77, 8.10 (4 H, dd, 1,4-disub. benzene ring); $\delta_C[(CD_3)_2SO]$ 14.23 (CH_2CH_3), 22.39, 24.26, 28.67, 28.87, 28.92, 29.11, 31.56, 37.92 (8 × CH_2), 24.06 (C-CH_3), 73.08 (C-CN), 119.49 (CN), 122.75, 130.99 (CH-aromatic), 133.78, 152.97 (C aromatic) and 166.81 (CO_2H); *m/z* 122.0329 [32.5, M – $C_9H_{19}C(CH_3)(CN)N_2$], 149.0346 [96.3, M – $C_9H_{19}C(CH_3)CN$], 180.1744 (2.5, M – $N_2C_6H_4CO_2H$).

Sodium 4-(2-cyanoundecan-2-ylazo)benzoate 4

A similar reaction to the above without acidification gave the salt **4**, 92%; ν_{max}/cm^{-1} 3065w, 2927w, 2857m, 2236w, 1601s, 1563s, 1422s, 1310m, 1094m, 887m, 871w, 841w, 794s, 728w and 700s; $\delta_H(CD_3OD)$ 0.88 (3 H, t, J 6, CH_2CH_3), 1.20–1.42 (12 H, m, 6 × CH_2), 1.43–1.62 (2 H, m, CH_2), 1.75 (3 H, s, C-CH_3), 2.04–2.30 (2 H, m, CH_2) and 7.76, 8.12 (4 H, dd, 1,4-disub. benzene ring). A reliable combustion analysis for **4** proved to be unobtainable and so the surfactant was fully characterized only as the acid **3**.

4-Alkylphenylazosulfonates

As all the sodium 4-alkylphenylazosulfonates were prepared similarly, the procedure for one compound, sodium 4-dodecylphenylazosulfonate **5**, is described below as representative of the general synthetic method.

Sodium 4-dodecylphenylazosulfonate 5. Sodium nitrite (1.00 g, 14.5 mmol) in water (6.6 ml) was added dropwise to a stirred suspension of 4-dodecylaniline (3.30 g, 12.6 mmol) in 3 M HCl (13.2 ml) while keeping the internal temperature between 0 and 5 °C. After further stirring at 0 °C for 20 min the solution was neutralized with sodium acetate, filtered and added to an ice-cold solution of sodium sulfite (3.17 g, 25.2 mmol) in water (20 ml). After the mixture had been left in the dark for 16 h, the precipitate was collected, washed with petrol and acetone and doubly recrystallized from boiling water to give **5** as a fine buff-coloured powder (0.75 g, 16%), mp 144–146 °C (Found: C, 57.6; H, 7.9; N, 7.3; S, 8.3. $C_{18}H_{29}N_2O_3SNa$ requires C, 57.4; H, 7.8; N, 7.4; S, 8.5%); ν_{max}/cm^{-1} (KBr) 3063w, 2958m, 2924s, 2854s, 1615w, 1522w, 1470s, 1295s, 1275s, 1234s, 1162w, 1079s, 904w, 853m, 822w, 760w, 729w and 657s; δ_H(CD$_3$OD) 0.90 (3 H, t, *J* 7, CH$_3$), 1.21–1.35 (18 H, m, 9 × CH$_2$), 1.64–1.67 (2 H, m, ArCH$_2$C*H*$_2$-), 2.71 (2 H, t, *J* 8, ArC*H*$_2$CH$_2$-) and 7.38, 7.81 (4 H, dd, 1,4-disub. benzene ring).

Sodium 4-decylphenylazosulfonate 6

Compound **6** was obtained in a yield of 28%, mp 151–152 °C (Found: C, 55.0; H, 7.3; N, 7.9; S, 9.2. $C_{16}H_{25}N_2O_3SNa$ requires C, 55.15; H, 7.2; N, 8.0; S, 9.2%); ν_{max}/cm^{-1} (KBr) 3051w, 2958m, 2924s, 2854s, 1609w, 1522w, 1470m, 1295s, 1244s, 1162w, 1079s, 1017w, 914w, 853w, 822w, 760w, 729w and 657s, δ_H(CD$_3$OD) 0.90 (3 H, t, *J* 7, CH$_3$), 1.28–1.35 (14 H, m, 7 × CH$_2$), 1.60–1.68 (2 H, m, ArCH$_2$C*H*$_2$-), 2.71 (2 H, t, *J* 8, ArC*H*$_2$CH$_2$-) and 7.37, 7.81 (4 H, dd, 1,4-disub. benzene ring).

Sodium 4-octylphenylazosulfonate 7

Compound **7** was obtained in a yield of 15%, mp 140–142 °C (Found C, 52.8; H, 6.8; N, 8.5; S, 9.8. $C_{14}H_{21}N_2O_3Na$ requires C, 52.5; H, 6.6; N, 8.7; S, 10.0%); ν_{max}/cm^{-1} (KBr) 3063w, 2959m, 2929s, 2856s, 1612w, 1515m, 1476m, 1321w, 1263s, 1234s, 1166w, 1069s, 1020w, 904w, 826m, 758w, 729w and 652s; δ_H(CD$_3$OD) 0.89 (3 H, t, *J* 7, CH$_3$), 1.29–1.35 (10 H, m, 5 × CH$_2$), 1.61–1.68 (2 H, m, ArCH$_2$C*H*$_2$-), 2.70 (2 H, t, *J* 8, Ar*H*$_2$CH$_2$-) and 7.38, 7.81 (4 H, dd, 1,4-disub. benzene ring).

Sodium 4-hexylphenylazosulfonate 8

Compound **8** was obtained in a yield of 29%, mp 155–157 °C (Found C, 49.1; H, 5.7; N, 9.6; S, 11.1. $C_{12}H_{17}N_2O_3SNa$ requires C, 49.3; H, 5.9; N, 9.6; S, 11.0%); ν_{max}/cm^{-1}(KBr) 3062m, 2969s, 2939s, 2862s, 1519m, 1475m, 1421w, 1267s, 1234s, 1168m, 1069s, 1025w, 959w, 905m, 850m, 839m, 762m, 729w and 652s; δ_H(CD$_3$OD) 0.90 (3 H, t, *J* 6, CH$_3$), 1.28–1.36 (6 H, m, 3 × CH$_2$), 1.60–1.68 (2 H, m, Ar CH$_2$C*H*$_2$-), 2.71 (2 H, t, *J* 7, ArC*H*$_2$CH$_2$-) and 7.37, 7.81 (4 H, dd, 1,4-disub. benzene ring).

Photolysis of sodium 4-octylphenylazosulfonate 7

A solution of **7** (5.62 × 10^{-3} M) was photolysed for 7 h. The aqueous solution was extracted with dichloromethane and was then acidified and exhaustively extracted with further dichloromethane. The organic extracts were combined, dried (Na$_2$SO$_4$) and evaporated under reduced pressure. Analysis by GC using anthracene as the internal standard showed the presence of 4-octylphenol **9** and 1-phenyloctane **10** in a ratio 1 : 3.1. A repeat reaction gave the products in the ratio of 1 : 3.6.

Emulsion polymerizations

All experiments were carried out in a fume-cupboard with exclusion of light. The azosulfonate surfactant (various mol % based on monomer) was added to deionized water (10.0 ml) and the mixture was placed, under nitrogen, in a thermostatted bath at the required temperature. To the stirred solution, monomer (1.0 ml) was added forming an emulsion. The initiator (various mol % based on monomer) was added and the reaction allowed to proceed. The results are summarized in Table 3, and in no case was a satisfactory polymerization achieved.

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