PHOTOCHEMICALLY INDUCED BREAKDOWN OF ROD-LIKE MICELLES: LIGHT-INDUCED VISCOSITY CHANGES

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Summary

The photochemical decomposition of three types of azo compound is used to change the viscosities of surfactant solutions. The azo additives are solubilized in systems containing rod-like cetyl-pyridinium salicylate micelles, and decomposed by UV irradiation. For solubilized 4-hexyl-phenyl-diazenium chloride, the viscosity reduces to 14% of its initial value after photolysis. Aryl-diazenium compounds suffer from thermal instability. Sodium 3-alkyl-phenyl-azoniumsulphonates, which are more stable in the solid phase and in aqueous solution, exhibit a strong tendency to decompose on contact with the micellar solution. In contrast, the compound 3-methyl-phenyl-azo-phenylsulphone is stable in the micelles. On UV irradiation the viscosity reduces to 6% of its value after solubilization. The concentration of azo additive required to produce the photorheological effect corresponds to one-seventh of the surfactant concentration. A quantum yield of 0.025 ± 0.002 has been determined for the photolysis at 308 nm in toluene and ethanol. On average, approximately 11 quanta per solubilized molecule are required to produce the viscosity breakdown. Gas chromatography–mass spectrometry (GC–MS) analysis reveals that alkyl-benzenes are the products of the photochemical reaction in the micellar system: these hydrocarbons decrease the viscosity, as they convert the rod-like micelles into small spherical aggregates.

1. Introduction

Photorheological effects in micellar solutions have recently produced considerable interest [1 - 4] in view of potential actinometric applications. Wolff and coworkers [2 - 4] have used the photochemical conversion between “rheologically active” and “inactive” forms of compounds solubilized in cetyl-trimethyl-ammonium-bromide or Triton X-100 micellar solu-

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tions. Typically, the "active" form increases the viscosity on solubilization. On photoconversion of the additive the viscosity decreases again, frequently because the photoproduct is poorly soluble in the micellar solution, and hence rheologically "inactive". Examples are the photodimerization of 9-anthracene derivatives [1], the cis → trans photoisomerization of 4-carboxystilbene [4], the photodecarboxylation of phenylglyoxylic acid, and the photocyclization of N-methyl-N,N-diphenylamine. In the last example, the less basic photoproduct (N-methyl-carbazole) is the rheologically active compound [4].

In this study we have followed a different approach, which is based on the work of Hoffmann and coworkers [5, 6]. Hoffmann and Ulbricht [5] have studied the solubilization of aliphatic and aromatic hydrocarbons in surfactant solutions. Concentrations of the surfactant (e.g. cetyl-pyridinium salicylate (CPySal)) are adjusted such that prior to any solubilization, rod-like micelles are present in the solution. On addition of small amounts of hydrocarbon, a swelling of the rods is observed due to solubilization. When the hydrocarbon concentration is increased above the solubilization capacity of the rods, a sudden breakdown of the viscosity is observed: light-scattering experiments reveal that the rods are decomposed, and small spherical micelles are formed [5]. Important for the present study is the fact that this rod → sphere transformation is induced by non-polar aliphatic compounds and by aromatic hydrocarbons carrying n-alkyl substituents; in contrast, polar additives such as alcohols do not destabilize rod-like micelles. The importance of the alkyl chain is demonstrated for tetradecyl-trimethylammonium salicylate micelles by a comparison of toluene and n-butylbenzene solubilization. While toluene solubilization results in a viscosity increase, the addition of n-butyl-benzene causes breakdown of the rods when a critical solute concentration is exceeded. The longer the alkyl chain, the smaller is the concentration required to induce the rod → sphere transformation. For the rod-like CPySal micelles investigated in this work, toluene is sufficiently non-polar to cause a breakdown of the rods at small solubilized concentrations, whereas substituted phenols such as m-cresol are rheologically inactive.

2. Strategy and reaction mechanism

From the evidence mentioned above, Hoffmann [7] has suggested a novel scheme to change the viscosity of a micellar solution. If a polar additive, solubilized in rod-like micelles, could be transformed into a non-polar compound by photochemical reaction, then the photoproduct would induce the rod → sphere transformation and cause a drastic decrease in the viscosity. In search for suitable systems to realize this idea, we have focused on the azo group \(-N=N-\) as the photolabile moiety. The reactions of substituted diazonium ions, \(R-C_6H_4-N=N^+\), were investigated. From studies in aqueous solution it is known [8] that the phenols \(R-C_6H_4-OH\) are the most abundant photoproducts. However, in the presence of reducing agents,
such as hypophosphoric acid, the reaction can be directed \[8\] towards the desired hydrocarbon \(R-C_6H_5\), which would cause the rod \(\rightarrow\) sphere transformation for \(R = n\)-alkyl. These experiments demonstrate the desired effect, as is discussed below, but the use of diazonium compounds is unsatisfactory due to their thermal instability.

To increase the stability of the solubilize, the diazonium group was replaced by the azosulphonate moiety. Results obtained with compounds of the type \(R-C_6H_4-\text{N=N-SO}_3^-\) are described in detail below, and a photochemical reaction scheme is proposed. The azosulphonates show high photo-rheological effects, but are still unsatisfactory with respect to stability. When the substituent \(R\) is in para position, the compounds are thermally unstable in aqueous solution. Meta-substituted azosulphonates are stable in water, but decompose spontaneously on contact with a micellar solution. Finally, we investigated substituted phenyl-azo-phenylsulphones, \(R-C_6H_4-\text{N=N-SO}_2-C_6H_5\), which are characterized by both thermal stability in micellar solutions and photochemical reactivity. For these compounds a mechanism of photolytic decomposition has been formulated \[9, 10\] and is discussed below.

3. Experimental details

3.1. Synthesis of the azo compounds

Diazonium salt solutions were prepared according to standard procedures \[11\]. The appropriately substituted aniline \(R-C_6H_4-NH_2\) (\(R \equiv \text{CH}_3, n-C_3H_7, n-C_4H_9\) or \(n-C_6H_{13}\) in either the meta or para position) was dissolved in 3 M hydrochloric acid at 0 °C; stoichiometric amounts of 2.5 M sodium nitrite solution were slowly added. The diazonium compound was characterized by its UV spectrum but not isolated; rather, the product solution was filtered and added directly to the surfactant system. (Warning. Diazonium compounds can be highly explosive. Consult the relevant safety instructions, as summarized in refs. 11 and 12.)

For the synthesis of azosulphonates, the hydrochloric acid solution of the corresponding diazonium compound was added to a solution containing \(\text{Na}_2\text{SO}_3\) (1.3 M) and sodium acetate (2.67 M) at \(-5\) °C, according to the procedure described in refs. 10 and 13. After removal of half the solvent under reduced pressure, the product crystallized overnight at 0 °C in the form of yellow-orange needles, and was purified by dissolving in ethanol at 35 °C, followed by recrystallization at room temperature.

3-Methyl-phenyl-azo-phenylsulphone was prepared \[9, 10\] in a similar manner by adding the hydrochloric acid solution of 3-methyl-phenyl-diazonium chloride to a solution containing \(C_6H_5-\text{SO}_2^-\text{Na}^+\) (benzene-sulphinic acid, sodium salt, 0.56 M) and sodium acetate (2.2 M) at \(-5\) °C. The solution was stirred at room temperature for 15 min; the product was crystallized overnight at 4 °C, and recrystallized from ethanol at 35 °C, as above.
3.2. Solubilization

Experiments were carried out at a final surfactant concentration of 20 - 50 mM; CPySal forms rod-like micelles in this concentration range [6]. The azo compound was added to a final concentration of 5 - 15 mM, as specified below.

3.3. Photocatalytic irradiation experiments

Decomposition experiments were carried out by irradiating the stirred solution, which was contained in a quartz tube, with a medium pressure mercury lamp (Hanau, model Hanovia L, 450 or 700 W).

For the determination of quantum yields an excimer laser (Lambda-Physik, model LPX 100) was used. The laser was operated at 308 nm (XeCl) and delivered pulses of approximately 100 mJ at a rate adjustable between 1 and 200 Hz. The rectangular beam profile (10 mm × 20 mm) was directed on to the front surface of a standard quartz cuvette containing the surfactant solution. The decomposition was monitored off-line by repeated measurements of the UV absorption after a given number of excimer pulses had been delivered. A conventional double-beam spectrometer (Perkin–Elmer, model Lambda 17) was used for recording the absorption spectra.

When larger volumes of solution (30 - 50 ml) were needed to measure the rheological properties as a function of UV radiation dose, the solution was stirred in a standard beaker, and irradiated with the excimer laser from the top. At the pulse rates used, no temperature rise of the solution was observed.

3.4. Rheological measurements

Viscosities were measured in a cone-plate viscosimeter (Contraves, models Rheomat 30 and Rheoscan 30, system 25). The rotation frequency was scanned from 0.1 to 6 Hz during 2 min. The value at 6 Hz is used throughout this work to compare the various solutions before and after irradiation, as standard deviations of measured viscosities were smallest at this frequency. Zero-shear viscosities were determined for selected solutions on a rheometric system (Chempro, Hanau, model OCR-D).

3.5. Gas chromatography–mass spectrometry (GC–MS) analysis

To prepare the irradiated solutions for GC–MS analysis, the surfactant component had to be removed. For this purpose, water was evaporated from the solutions under reduced pressure. A small volume of an acetone–n-hexane mixture (1:1) was added. The solution was stored at 4 °C, and crystalline surfactant was repeatedly removed by filtration. Finally, the solution was diluted with benzene prior to injection into the gas chromatography–mass spectrometry (GC–MS) analysis.
graph (Hewlett-Packard, model 5890, equipped with a flame ionization
detector (FID)). "Ultra 1" and "Ultra 2" columns (25 m) were used. Mass
spectra were recorded on a Hewlett-Packard instrument (model MSD
5970).

4. Results

4.1. Solubilization of 4-alkyl-aryl-diazonium chlorides

As mentioned above, phenols are formed by the decomposition of
aromatic diazonium halides in aqueous solution [8]. To form a hydrocarbon
photoproduct, reducing agents must be added in homogeneous solution.
Therefore the first set of experiments was performed with systems con-
taining the surfactant (CPySal, 20 mM), 4-butyl- or 4-hexyl-diazonium
chloride (20 mM), hypophosphoric acid (H₃PO₂, 60 mM) and HCl (100 mM).
However, it was found that the viscosity of the solution was considerably
decreased (by more than 50%) during the H₃PO₂ addition, such that subse-
quent irradiation produced only a limited effect.

The spectral characteristics of this system are shown in Fig. 1. The
aqueous solution of 4-butyl-phenyl-diazonium chloride (Fig. 1(a)) exhibits a
maximum at 280 nm. (A precise determination of the extinction coefficient
was not feasible as the diazonium compound was not isolated from the

\[ \text{wavelength / nm} \]

\[ \text{absorbance} \]

Fig. 1. UV photolysis of 4-butyl-phenyl-diazonium chloride. (a) Absorption spectrum of
an aqueous solution. (b) UV spectrum of a 12 mM solution of 4-butyl-phenyl-diazonium
chloride in 40 mM CPySal, diluted by a factor of 100 (trace (i)). Irradiation with 500
pulses (100 mJ each) from an excimer laser results in a pronounced decrease in the
diazonium absorption at 285 nm, as shown in trace (ii).
reaction mixture. An extinction coefficient $\epsilon \approx 15\,000\,\text{M}^{-1}\text{cm}^{-1}$ has been reported for \textit{para}-substituted benzene-diazonium chlorides \cite{12}. The CPySal surfactant system is characterized by strong absorptions at 235 nm and 260 nm, and a weaker band at 295 nm. For the solution of 4-butyl-diazonium chloride in the CPySal system (Fig. 1(b)), a superposition of the above-mentioned absorptions is visible. On irradiation with 500 excimer laser pulses (of 100 mJ each) at 308 nm, a strong decrease in the diazonium absorption at 280 nm is clearly observed; the residual long-wavelength peak at 295 nm is due to the surfactant.

As a next step, we tried to include the reducing agent into the surfactant system itself: some of the salicylate counter-ions were replaced by the anion of 2,5-dihydroxy-benzoic acid, which is easily oxidized. A solution containing 40 mM cetyl-pyridinium chloride, 30 mM sodium salicylate (2-hydroxy-benzoate) and 10 mM 2,5-dihydroxy-benzoic acid exhibited a remarkable viscoelastic behaviour: several periods of oscillation were observed after shaking a standard laboratory flask. A zero-shear viscosity of 1700 mPa s and a viscosity of 33 mPa s at 6 Hz were determined for this system. 4-Butyl-diazonium chloride was added to this solution at a concentration of 20 mM. On UV irradiation of the solution with the mercury lamp in the set-up described above, nitrogen evolution ceased after 30 min, and the solution had a clear, water-like, non-viscous appearance. The final viscosity was 10 mPa s, \textit{i.e.} 30\% of the starting value.

Finally, a test series was performed in which the reducing agents were completely omitted. To our surprise, these solutions exhibited the largest, both absolute and relative, photoinduced viscosity changes of all the systems discussed so far. The concentration of CPySal was adjusted to 40 mM. When 15 mM of 4-butyl-diazonium chloride was solubilized and then irradiated, the viscosity (measured at 6 Hz) decreased to 19\% of its starting value. For the same concentration of 4-hexyl-diazonium chloride, the decrease was even stronger: a final viscosity of 5 mPa s (14\% of the starting value) was reached after 25 min of irradiation (Fig. 2).

These observations suggest that the radical reaction takes a different course in the micelles than in aqueous solution, where rheologically inactive phenols are formed. To clarify this point, GC–MS analysis of the product solutions was performed. Main products from the photolysis of 4-butyl-diazonium chloride in CPySal solution were identified as 4-butyl-phenol and 4-butyl-benzene, with a GC area ratio of 1:1.2. From the irradiation of 4-hexyl-diazonium chloride in CPySal, 4-hexyl-phenol and 4-hexyl-benzene were obtained with an area ratio of 1:8. Thus it appears that, contrary to the behaviour in aqueous solution, the hydrocarbon is formed when the diazonium ion is photolysed in CPySal micelles. The hydrocarbon product is favoured more strongly for the more lipophilic hexyl-substituted compound. The 4-alkyl-phenyl radical \cite{14} formed after nitrogen elimination may abstract a hydrogen atom from the surfactant, or possibly react with the salicylate counter-ion.
Fig. 2. Viscosity changes induced by decomposition of solubilized azo compounds. The surfactant solution contained rod-like micelles of CPySal at a concentration of 40 mM. The sodium salts of 3-methyl-phenyl-azosulphonate (3-MPAS), 3-propyl-phenyl-azosulphonate (3-PPAS), 3-butyl-phenyl-azosulphonate (3-BPAS) and 4-hexyl-phenyl-diazonium chloride (4-HPDCl) were added in quantities corresponding to a final concentration of 15 mM. The compounds 3-MPAS and 3-BPAS were added in solid form. (Note that 3-MPAS and 3-PPAS decompose with nitrogen evolution on contact with the micellar solution.) Systems containing 3-BPAS and 4-HPDCl were irradiated with a UV lamp to complete degradation (see text). (a) Viscosities of the systems measured at 6 Hz prior to solubilization ($\eta_i$, light bars) and after complete decomposition ($\eta_f$, dark bars). (b) The relative viscosity change $Q = \eta_f/\eta_i$.

In summary, the solubilization and subsequent UV irradiation of diazonium compounds unambiguously results in the desired viscosity change induced by the photoproducts. However, these systems are not suited for practical applications due to their thermal instability: when a solution of 4-butyl-phenyl-diazonium chloride in CPySal is stored in the dark at room
temperature, the half-life of the diazonium compound is approximately 7 h, as determined from UV spectroscopy. Thermal decomposition produces the same viscosity breakdown as observed on UV irradiation.

4.2. Solubilization of n-alkyl-phenyl-azosulphonates

As a starting point, the thermal stability of the compounds in homogeneous aqueous solution was investigated by monitoring the UV spectrum. The para-substituted compounds proved to be unstable over a time scale of hours. Irradiation of fresh solutions resulted in facile photocleavage, with the corresponding phenol detected as the main product in the UV spectrum (absorption at 220 nm, Fig. 3(a)).

Attempts to increase the stability of the azosulphonates by introducing a σ or π acceptor (e.g. a nitro group) into the aromatic ring were unsuccessful, as the corresponding products were no longer soluble in water. As an alternative, we reduced the σ-donor effect of the n-alkyl group, by attachment in the meta rather than the para position with respect to the azo group. This approach gave a series of compounds which were stable in aqueous solution at room temperature: for solutions of the sodium salt of 3-methyl-phenyl-azosulphonate (3-MPAS) no change in the UV spectrum was observed during 15 h.

![Graphs showing UV spectra changes](image-url)

Fig. 3. Photochemically-induced changes in the UV spectra of an aqueous solution of 4-butyl-phenyl-azosulphonate (a) and an ethanolic solution of 3-methyl-phenyl-azo-phenylsulphone (b). Between successive traces, the cuvette was irradiated with sets of five excimer laser pulses (of 90 mJ each) at 308 nm at a rate of 1 Hz.
Interestingly, the stability of 3-MPAS is drastically decreased in the presence of CPySal micelles. When a solution of 3-MPAS is added to a 40 mM CPySal solution, instantaneous decomposition of the azo compound is observed, and the viscosity decreases to 5% of its starting value (Fig. 2). Apparently the compound, which is stable in homogeneous solution, decays spontaneously at the micellar interface, a phenomenon that has been observed for other systems [15].

We attempted to increase the stability in the micelles by replacing the methyl group by longer chain substituents. 3-Propyl-phenyl-azosulphonate (3-PPAS) is still soluble in water. When the crystalline compound is added to a 40 mM CPySal solution, spontaneous decomposition accompanied by nitrogen evolution is observed within approximately 60 s. As with 3-MPAS, the viscosity decreases to 5% of its starting value (Fig. 2).

The next homologue, 3-butyl-phenyl-azosulphonate (3-BPAS), is insoluble in water. However, 3-BPAS is the first compound in the homologous series which is not decomposed when the crystalline material (in quantities corresponding to a concentration of 15 mM) is added to a stirred CPySal solution. No homogeneous solution is achieved, i.e. the surfactant solution remains turbid due to suspended orange crystallites of 3-BPAS. When this dispersion is irradiated with the mercury lamp for 150 min in the quartz tube, a modest decrease in viscosity (50%) is observed (Fig. 2).

As 3-BPAS produces the desired photoinduced viscosity change, although not as strongly as the diazonium compounds, the product solution was analysed by GC–MS: the only photoproduct observed was butylbenzene. As with the diazonium compounds, this behaviour should be contrasted with the photochemical decomposition in aqueous solutions, where the corresponding phenol is identified as the product from UV spectroscopy of water-soluble representatives (e.g. 4-BPAS, cf. Fig. 3(a)). These observations can be summarized as follows. In water, ionic cleavage prevails, which results in a substituted phenol product. In contrast, the substituted benzene is produced in micellar solution, which most probably arises from a radical decomposition mechanism (see Scheme 1).

We tried to overcome the insolubility of 3-BPAS by using the azosulphonate as the counter-ion of the micellar system instead of the salicylate ion. However, attempts to dissolve solid mixtures of cetyl-pyridinium chloride and sodium 3-butyl-phenyl-azosulphonate were not successful. In contrast with salicylate, the 3-BPAS anion apparently does not solubilize well in the micellar palisade layer formed by the pyridinium rings.

4.3. Solubilization of 3-methyl-phenyl-azo-phenylsulphone

3-Methyl-phenyl-azo-phenylsulphone (3-MPAPS) is the first compound prepared in this work that meets the requirements of stability in organic solvents and micellar solutions and photochemical degradability to rheologically active products. Therefore experiments with 3-MPAPS are described in more detail.
Stability was checked by monitoring the constancy of the UV spectrum with time. Next, the concentration of 3-MPAPS required to induce the breakdown of rods and a concomitant large viscosity change was determined, with the surfactant concentration (CPySal) held constant at 40 mM. The solution (50 ml) was stirred in an open beaker, and was irradiated with 100 mJ pulses from an excimer laser operated at 308 nm. Completeness of photochemical decomposition was inferred from the disappearance of the parent compound absorption in the UV spectrum, as shown in Fig. 3(b). For each system, we determined the initial viscosity $\eta_i$ (measured at 6 Hz), the somewhat lower viscosity $\eta_s$ after 3-MPAPS solubilization and the final viscosity $\eta_f$ after exhaustive irradiation (Fig. 4(a)).

Results are presented in Fig. 4(b) as the ratios $Q = \eta_f/\eta_i$ (light bars) and $Q' = \eta_f/\eta_s$ (shaded bars): obviously the ratio $Q'$ is somewhat larger than $Q$. From the figure and additional experiments, $Q'$ shows a decrease from approximately 0.10 to about 0.07 as the concentration of the solubilizate (3-MPAPS) is decreased from 15 mM to 6 mM; this implies that the relevant relative viscosity change is largest when the 3-MPAPS concentration is chosen at the lower limit of the indicated interval. However, with a further decrease in the 3-MPAPS concentration to 5 mM, the photorheological effect is much less pronounced, and the final viscosity remains as high as 58% of the starting value. For this system, insufficient photoproduct (toluene) is produced to induce the rod $\rightarrow$ sphere transition. Summarizing the results of
Fig. 4. Viscosity changes in CPySal micellar systems (40 mM) induced by photochemical decomposition of solubilized 3-methyl-phenyl-azo-phenylsulphone (3-MPAPS). The concentration of 3-MPAPS was varied. (a) Viscosities measured at 6 Hz prior to solubilization ($\eta_s$, light bars), after solubilization ($\eta_i$, shaded bars) and after photodecomposition ($\eta_f$, dark bars). (b) Relative viscosity changes $Q = \eta_f/\eta_i$ (light bars) and $Q' = \eta_f/\eta_s$ (shaded bars).

Fig. 4, it can be seen that for the surfactant system studied (40 mM CPySal), a solubilize concentration of 6 mM is optimal: it produces the least perturbation of the initial viscoelastic solution ($\eta_s \approx 0.75\eta_i$), and yet is sufficient to destroy the micellar rods after photolysis.

At this point it is worthwhile to comment on the validity of the structural model which was used to interpret the observed viscosity changes. Unfortunately, light-scattering measurements are not feasible with the
deeply coloured solutions containing theazo derivatives. However, we can draw conclusions from the absolute viscosity values observed, by comparing them with those of the pure CPySal system for which extensive light-scattering measurements have been performed [5]. Referring to Fig. 4(a) it can be seen that the viscosities after 3-MPAPS solubilization, i.e. 20 - 32 mPa s, are clearly in the range where the existence of rod-like micelles has been established for the surfactant. However, the low value of the viscosity after irradiation (2 mPa s) unambiguously shows that the rods have been destroyed. As the surfactant concentration is well above the critical micelle concentration (CMC), spherical micelles must be present in the solution.

In the 3-MPAPS-CPySal system, a quantitative separation of the photoproducts from the surfactant system prior to GC–MS analysis is difficult due to the comparatively high solubility of m-cresol and toluene in water. In agreement with the results obtained with the azosulphonates, we detected 3-hydroxy-toluene and toluene as the main products from photolysis in aqueous and micellar phases respectively.

A series of experiments was performed to test whether the indicated results are independent of surfactant concentration in the range where rod-like micelles exist in solution. Although the absolute viscosity $\eta_l$ increases with increasing CPySal concentration as expected, the ratios $Q$ and $Q'$ defined above remain constant within ±0.01. This is demonstrated by the sample set of data in Table 1.

<table>
<thead>
<tr>
<th>CPySal concentration (mM)</th>
<th>3-MPAPS concentration (mM)</th>
<th>$Q = \eta_l/\eta_o^a$</th>
<th>$Q' = \eta_l/\eta_s^a$</th>
</tr>
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<tbody>
<tr>
<td>40</td>
<td>10</td>
<td>0.06</td>
<td>0.09</td>
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<tr>
<td>50</td>
<td>10</td>
<td>0.04</td>
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<tr>
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<tr>
<td>50</td>
<td>7.5</td>
<td>0.05</td>
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$^a$ Standard deviation, ±0.01.

Zero-shear viscosities $\eta_0$ were also determined for this system. Prior to solubilization a value $\eta_{0,i} = 550$ mPa s was measured for a 40 mM CPySal solution. After solubilization of 3-MPAPS at a concentration of 7.5 mM, $\eta_0$ decreased to $\eta_{0,s} = 24$ mPa s. Finally, the photochemically-induced rod → sphere transition reduced $\eta_0$ to a value $\eta_{0,i} = 1.1$ mPa s, which is close to the viscosity of water ($\eta_0 = 1.0$ mPa s). Hence, the effect of photochemically-induced viscosity breakdown is also quite pronounced when expressed by zero-shear viscosities, i.e. $\eta_{0,i}/\eta_{0,s} = 0.046$. 


4.4. Quantum yields of photochemical decomposition and viscosity change

Quantum yields of photodegradation were determined by measuring the decrease in UV absorption as a function of the number of excimer pulses delivered. The solution was contained in a standard 10 mm × 10 mm quartz cuvette; initial concentrations were adjusted such that all incident photons were absorbed, except for the very latest stages of the decay. From the measured energy per laser pulse, quantum yields of the photoreaction were determined.

As an example, the UV spectra recorded during decomposition of an aqueous solution of 4-butyl-phenyl-azosulphonate are shown in Fig. 3(a). Between subsequent traces, five excimer laser pulses at 308 nm (of 90 mJ each) were delivered to the sample at a rate of 1 Hz. Apparently only one photoproduct is formed, as evident from the observation of two isosbestic points.

Similar results for the photochemical decomposition of 3-MPAPS are shown in Fig. 5. The plot of absorbance against fluence (energy per pulse multiplied by the number of pulses delivered) is linear as the absorption of incident photons is essentially complete. In toluene, a quantum yield of 0.023 is determined for the decomposition at 308 nm; in ethanol the corresponding value is 0.025 ± 0.002.

![Fig. 5. Quantum yields of photochemical decomposition. The absorbance of a 3-MPAPS solution in toluene (*) and ethanol (□) vs. the total energy (λ = 308 nm) deposited in the sample. (Note that the solutions essentially absorb all the incident photons for the part of the decay which is shown.)](image)

Determination of a "quantum yield" for the viscosity change requires some caution as the viscosity is not a linear function of the number of hydrocarbon molecules produced [5]. Extended solubilization times are required to obtain reproducible results. A 6 mM solution of 3-MPAPS in 40 mM CPySal was stirred for 24 h at room temperature. The solution (50 ml) was then irradiated with the excimer laser from the top. The viscosity was measured repeatedly after sets of 2000 or 4000 laser pulses had
been delivered to the sample at a pulse rate of 2 Hz and an energy of approximately 120 mJ per pulse. The viscosity exhibited a decrease with total energy $E$ that roughly followed an exponential behaviour, $\eta(E) = \eta(0) \exp(-aE)$. Data from three typical runs are shown in Fig. 6. For the volume and concentrations specified above, $1075 \pm 125$ J of laser energy are required to decrease the initial viscosity by a factor of e. This corresponds to $1.7 \times 10^{21}$ photons incident on a solution which contains $1.8 \times 10^{20}$ molecules of the solubilizate (3-MPAPS) and $1.5 \times 10^{21}$ surfactant molecules. Thus the "quantum yield" for the viscosity change is approximately 0.09, i.e. on average 11 photons must be delivered per solubilized molecule to induce the rod $\rightarrow$ sphere transition.

The quantum efficiency of the viscosity change is somewhat higher than that of the photochemical decomposition in homogeneous solution (0.025); two reasons can be indicated for this observation. Firstly, our experience with the diazonium and azosulphonate compounds indicates that nitrogen is produced more readily when the compounds are solubilized in the micelles, as mentioned above. Secondly, not all solubilized molecules are decomposed at the instant when the viscosity breakdown occurs, which results in a higher apparent quantum yield.

![Fig. 6. Viscosity changes of a 6 mM solution of 3-MPAPS in 40 mM CPySal during irradiation with 120 mJ pulses from an excimer laser operated at 308 nm at a pulse rate of 2 Hz. The change in viscosity $\eta$ relative to the value after 3-MPAPS solubilization $\eta_0$ vs. the total energy deposited in the sample (three independent experimental runs ($\circ$, *, +)).](image)

5. Conclusions and outlook

The concept of light-induced viscosity change by photochemically-induced breakdown of rod-like micelles has been successfully realized using 3-methyl-phenyl-azo-phenylsulphone as the solubilizate. This compound is thermally stable both in aqueous and micellar solutions. About 11 quanta of 308 nm radiation per solubilized azo molecule are required to trigger the
viscosity breakdown. This high sensitivity suggests that the present system could be optimized for use in actinometric applications.

An interesting result of the GC-MS analysis is that diazonium, azosulphonate and azo-phenylsulphone photochemistry takes a different course when the compounds are solubilized in a micellar solution prior to irradiation. While in aqueous solutions the respective substituted phenols are produced, the corresponding alkyl-benzenes are the most abundant products in the micellar solution. For the azosulphonates and azo-phenylsulphones, this may indicate that a radical decomposition mechanism prevails in the micellar environment.

As an extension of this work, we are currently considering the synthesis of surfactant-type molecules which can be photochemically modified to exhibit similar photoinduced viscosity changes. As mentioned above, the compound sodium 3-butyl-phenyl-azosulphonate synthesized in this study is insoluble in water. Replacing the butyl substituent with a considerably longer (C_{10} - C_{14}) alkyl chain might be a viable route to obtain an azo derivative with the desired amphiphilic properties.

Acknowledgments

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References