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Spectroscopic and photochemical studies of xanthene and azo dyes on surfaces: cellophane as a mimic of paper and cotton

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Abstract

Steady-state UV–visible absorption spectra of a xanthene dye, Acid Red 52, and an azo dye, Direct Blue 1, have been studied in aqueous solution, on paper (Acid Red 52) or cotton (Direct Blue 1), and in cellophane films. Distinct spectral changes are observed when these dyes are deposited from solution on to paper or cotton, and the respective spectral changes are replicated on incorporation into a cellophane film. Dye photofading has also been studied in these media: the photofading of Acid Red 52 and Direct Blue 1 in solution was found to be very slow, with a low quantum yield; the photofading of each dye was significantly faster on paper or on cotton; and the photofading of each dye in cellophane was found to be significantly faster than in solution and similar to that on paper or cotton. Similar spectral changes were observed during the photofading of Acid Red 52 in cellophane and on paper, and of Direct Blue 1 in cellophane and on cotton. These similarities, both in steady-state spectra and in photofading properties, show that cellophane can be used as a good mimic for studying dye fading on paper or cotton; loading into cellophane is straightforward and it has the additional advantage, for spectroscopic studies, of being transparent. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Good lightfastness is paramount in numerous applications of dyes but some of the most intense colours are given by dyes which are prone to rapid photofading on surfaces. The rate of photofading may depend on external parameters such as the presence or absence of oxygen, moisture, or other additives. In addition, dyes bound to a surface may photofade with different rates on different surfaces, and the fading may be different from that in solution. In order to understand these effects, and to create more stable dyes, it is important to develop an understanding of the photofading processes.

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Different dye classes, and even different dyes within the same class, can fade with different mechanisms: the problem of determining a dye-photofading mechanism is non-trivial.

There are several possible methods for investigating dye fading. The most convenient method is to study the dyes in solution, where simple UV–visible absorption spectra may be used to monitor the fading process: this approach will yield useful information on the mechanism of dye fading in solution. However, the applicability of this information to surface photochemistry may be limited because the photochemical mechanism on a surface can be significantly different from that in solution: it is well known that many dyes fade faster on a surface than in solution [1].

Another method is to study dyes on surfaces. However, in order to study a dye on an opaque substrate such as fabric or paper, it is necessary to use reflectance spectroscopy. This approach can involve the relatively simple use of a spectral densitometer to measure values at fixed wavelengths, yielding tristimulus values [2]. Alternatively, full-range UV–visible diffuse reflectance spectra can be measured using an integrating sphere and a spectrophotometer. However, it may not be straightforward to compare two different substrates quantitatively using these techniques because the data can depend on factors such as the surface roughness and ‘scattering length’ [2]. In addition, the sampling arrangements for diffuse reflectance techniques often are less flexible than those for transmission techniques.

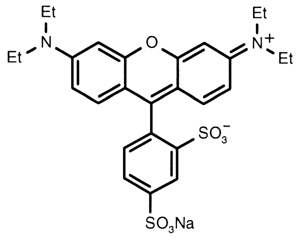
A more convenient method than reflectance studies of opaque surfaces would be to use a transparent medium which mimics the opaque materials of interest and, ideally, enables different dyes to be compared in the same medium using standard UV–visible absorption spectroscopy. Cellophane is a transparent film which can be studied by transmission techniques and might serve this purpose; furthermore, like cotton and paper, cellophane is a form of cellulose. The solid-state photochemistry of several systems, including methyl viologen [3–5] and some dyes [6,7], have been reported using cellophane as the matrix.

The work reported here was aimed at exploring the applicability of cellophane as a mimic for paper and cotton in dye photofading studies. We have studied two dyes: Acid Red 52 (Sulforhodamine B), which is a magenta dye used in inks, and Direct Blue 1 (Chicago Sky Blue 6B), which is used for dyeing cotton. The spectroscopy and photochemistry of these dyes have been studied here in solution, on their functional substrates (paper and cotton, respectively), and in cellophane. The results of both steady-state spectroscopic and photofading studies indicate that cellophane can provide a good mimic of paper and cotton for detailed studies of dye fading.

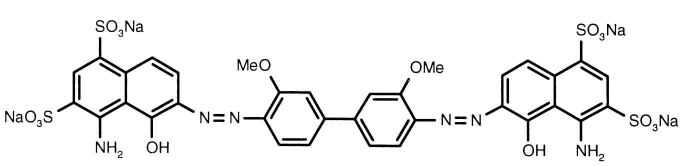
2. Experimental

2.1. Materials and methods

Acid Red 52 was supplied by Avecia; Direct Blue 1 (Aldrich) was recrystallised from water and ethanol. All solutions were prepared using deionised water: solutions of Acid Red 52 were adjusted to pH 9 by the addition of NaOH; solutions of Direct Blue 1 were used as prepared. Small (ca. 1×2 cm) pieces of cellophane sheet (Aldrich, thickness 45 μm) were dyed by soaking



Acid Red 52



Direct Blue 1

in a dye solution (typically 1–5×10^{-3} mol dm^{-3}) for 30 min, and were then dried between lint-free lens tissues; a weight was placed on top to prevent wrinkling of the cellophane as it dried. Paper samples were prepared by pipetting 4 μl of dye solution (typically 10^{-4} mol dm^3) onto a small (ca. 1×2 cm) piece of paper, spreading this out evenly into an 8-mm diameter spot, and then allowing it to dry. Dyed cotton samples were prepared by adding 15×15 cm pieces of desized, mercerised, non-fluorescent cotton to 1 l of water at 40°C; solid dye was added and the dyebath heated to 95°C; NaCl was then added at 10 g l^{-1}, and the dyebath was stirred at 95°C for a further hour; the samples were then rinsed and air-dried. The dye loading was determined as ca. 0.5 mg dye/g cotton. The pieces of fabric were cut into smaller (ca. 1×2 cm) pieces for the irradiation experiments.

Steady-state irradiation experiments were performed using either the 568.2 or 647.1-nm lines from a Kr+ ion laser (Coherent Innova 90): the beam was expanded to an 8-mm spot at the sample, and the power was adjusted to 100 mW; solution samples were held in a sealed 1-cm quartz cuvette and were stirred during the exposure. UV–visible transmission spectra of solutions and of cellophane films were recorded on a Hitachi U-3000 spectrophotometer; non-dyed cellophane was used as a reference when recording spectra of the films. UV–visible diffuse reflectance spectra were recorded on a Perkin–Elmer Lambda-15 spectrophotometer fitted with an integrating sphere, and are reported in Kubelka–Munk units which are proportional to sample concentration [2]; non-dyed paper and non-dyed cotton were used as the references when recording spectra of the paper and cotton samples, respectively.

2.2. Analysis

A quantitative comparison between different dyes and different samples is best made by calculating the quantum yield of photofading, which, unlike the observed photofading rates, is independent of dye concentration and irradiation power. The use of a laser to provide monochromatic irradiation enabled the quantum yield of fading, ϕ_{fade}, to be estimated readily: this was done by considering the initial fading rate, such that the change in the sample absorbance was small during the period concerned. The laser wavelength and power were used to calculate the number of photons incident on the sample per second, and this was then multiplied by the time over which the quantum yield was to be determined to give the total photon dose; the absorbance of the sample at the laser wavelength was then used to determine the number of photons absorbed by the sample. The total number of dye molecules irradiated was determined from the dye concentration and the volume irradiated, and the decrease in absorbance during the period concerned was used to determine the number of dye molecules bleached by the incident photons. The quantum yield is the ratio of the number of molecules bleached to the number of photons absorbed by the sample.

3. Results

3.1. Steady-state spectra

Figs. 1 and 2 show UV–visible spectra of Acid Red 52 in solution, on paper, and in cellophane, at different concentrations. At low concentration (Fig. 1), the spectra have similar profiles but closer inspection reveals differences. On going from solution to paper, the visible absorption maximum at 564 nm shows a red-shift of ca. 4 nm, and the spectrum shows less detail in the UV region; on going from solution to cellophane, the visible absorption maximum shows a red-shift of ca. 3 nm, and the spectra are more comparable in the UV region. On going to higher concentration in solution (Fig. 2), the spectrum of Acid Red 52 shows a strong new absorption feature at 528 nm. Similar, weaker new features are observed from the paper and cellophane samples; the bands in the diffuse reflectance spectrum of the paper sample are broadened significantly. As with the spectra recorded at lower concentration, the absorption maxima show red-shifts of ca. 3–7 nm on going from the solution to the paper and cellophane samples.

Fig. 3 shows UV–visible spectra of Direct Blue 1 in solution, on cotton, and in cellophane. There

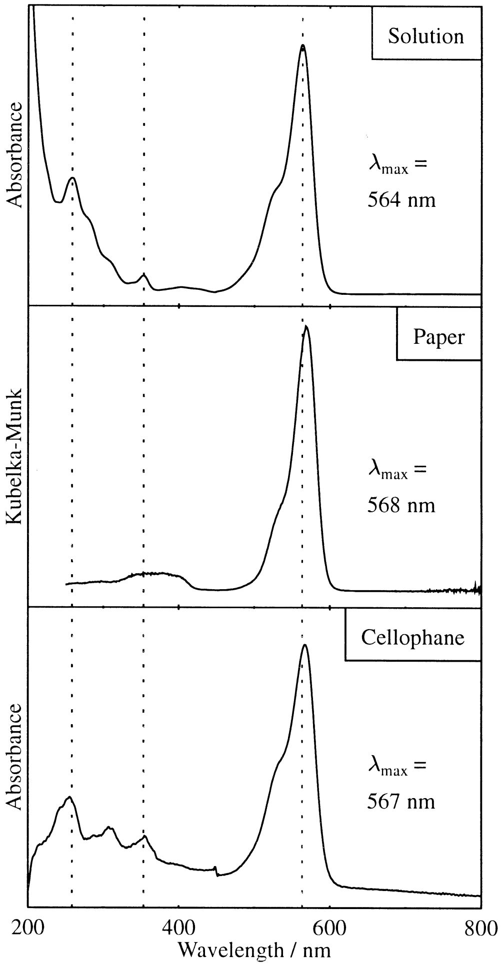


Fig. 1. UV–visible spectra of Acid Red 52 in solution, on paper, and in cellophane, at low concentration: 10^{-5} mol dm^{-3}, 10^{-4} mol dm^{-3} loading, and 10^{-3} mol dm^{-3} (concentration of parent solution), respectively.

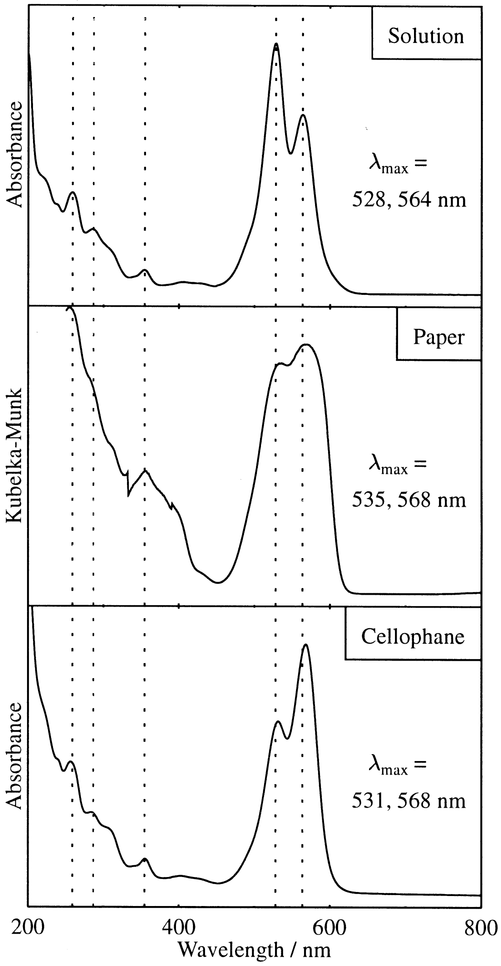


Fig. 2. UV–visible spectra of Acid Red 52 in solution, on paper, and in cellophane, at high concentration: 10^{-2} mol dm^{-3}, 10^{-2} mol dm^{-3} loading, and 2×10^{-3} mol dm^{-3} (concentration of parent solution), respectively.

are relatively large changes in the spectral profile on going from solution to cotton, or to cellophane. Most notably, the spectra of both cellophane and cotton samples show a new absorption feature at ca. 655 nm on the long-wavelength side of the visible absorption band. Absorption spectra of Direct Blue 1 solutions with higher concentrations show a new absorption feature on the blue side of the visible absorption band, similar to the effect observed for Acid Red 52, although the new feature is not resolved distinctly from the main absorption band.

3.2. Photofading studies of Acid Red 52

Fig. 4 shows a series of UV–visible spectra of Acid Red 52 in solution, on paper, and in cellophane, recorded during irradiation at 568.2 nm. The changes for the solution sample are extremely small (Δabsorbance <0.01), show no consistent trend, and are of the same order of magnitude as the error in the measurement. However, the magnitude of these spectral changes allows an upper estimate of the quantum yield of fading to be estimated. Under the experimental conditions used to

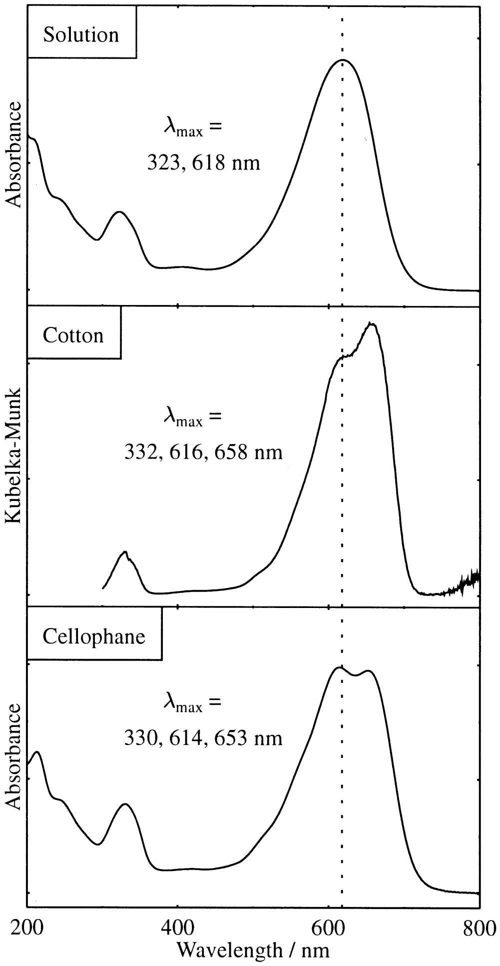


Fig. 3. UV–visible spectra of Direct Blue 1 in solution, on cotton, and in cellophane, at concentrations of 10^{-4} mol dm^{-3}, ca. 0.5 mg dye/g cotton loading, and 5×10^{-3} mol dm^{-3} (concentration of parent solution), respectively.

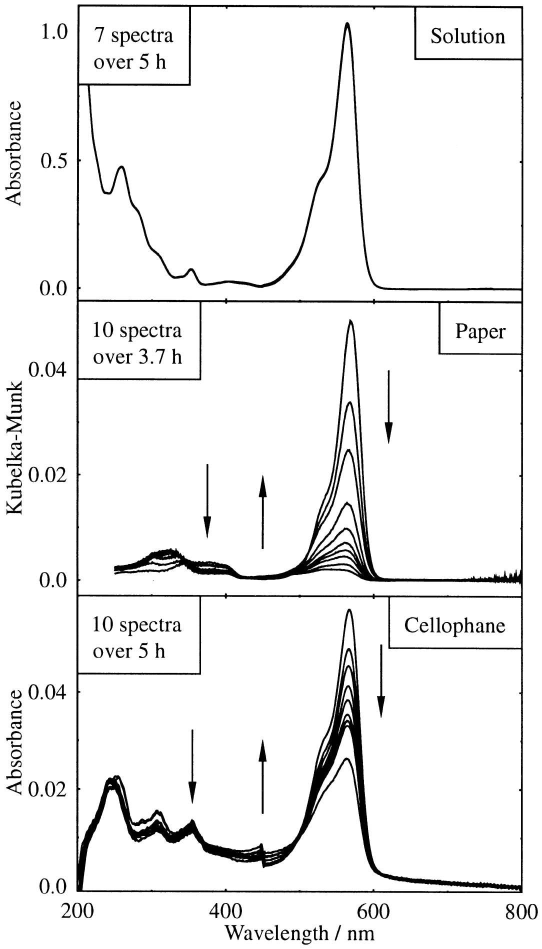


Fig. 4. UV–visible spectra of Acid Red 52 in solution, on paper, and in cellophane, recorded during 568.2-nm irradiation.

record the data from solution presented in Fig. 4, a change in absorbance of < 0.01 corresponds to a loss of $< 3\times10^{14}$ molecules over the 5 h irradiation period, during which 4.6×10^{21} photons were absorbed by the sample. This gives an upper limit for the quantum yield of fading in solution of $\phi_{\text{fade}} < 6 \times 10^{-8}$, i.e. the probability of an absorbed photon leading to a decomposed dye molecule is less than 6×10^{-8}.

The UV–visible diffuse reflectance spectra of Acid Red 52 on paper recorded during 3.7 h irradiation at 568.2 nm show rapid fading, accompanied by the growth of a weak band at ca. 450 nm; this new absorption feature is observed by eye as 'yellowing' as the magenta colour is lost. The fading is strikingly faster than that in solution but the observed rate depends on the total number of dye molecules present in the sample, and this is significantly lower than for the solution sample. A comparison can be made with the solution sample by estimating the quantum yield of fading from the initial fading rate. A 32% change in Kubelka–Munk at the absorption maximum corresponds to a loss of 7.7×10^{13} molecules over the initial 10 min of irradiation, during which 4.7×10^{19} photons were absorbed. This gives an estimated quantum yield on paper of $\phi_{\text{fade}}=2\times10^{-6}$, an increase in fading efficiency of more than ×30 when the dye is placed on to a paper substrate from solution. The fade over this initial period is large, and ϕ_{fade} estimated over an even shorter period may be even higher because of the decrease in sample absorption during this time.

The UV–visible absorption spectra of Acid Red 52 in cellophane, recorded during 5 h irradiation at 568.2 nm also show rapid fading. The spectral changes on fading in cellophane are similar to those on paper, including the growth of a weak band at ca. 450 nm. The estimated quantum yield of fading in cellophane is $\phi_{\text{fade}}=1\times10^{-6}$, calculated from the change over the first 10 min of irradiation; this is similar to that for fading on paper.

3.3. Photofading studies of Direct Blue 1

Fig. 5 shows a series of UV–visible spectra of Direct Blue 1 in solution, on cotton, and in cellophane, recorded during irradiation at 647.1 nm. In contrast to Acid Red 52 in solution, Direct Blue 1 in solution does fade progressively under these conditions, albeit very slowly, with an estimated quantum yield in solution of $\phi_{\text{fade}}=4\times10^{-7}$.

The UV–visible diffuse reflectance spectra of Direct Blue 1 on cotton recorded during 3 h irradiation at 647.1 nm show very rapid fading: a loss of ca. 15%, measured at the absorption maximum of 656 nm, occurs within the first minute of irradiation. The fading of this sample is significantly faster than that in solution, and it is notable that the absorption feature at 656 nm fades faster than the other main visible absorption band at ca. 620 nm; there is a slight colour change from blue to purple during the initial stages of photofading. The estimated quantum yield for fading of Direct Blue 1 on cotton is $\phi_{\text{fade}}=2\times10^{-5}$, calculated from the change at 656 nm over the first minute of irradiation; this wavelength shows the largest changes and therefore will yield the highest estimate of the quantum yield for fading. In contrast, there is hardly any change in the region near 550 nm at the earliest times and, for this dye, it is clear that the wavelength used to estimate such quantum yields is important.

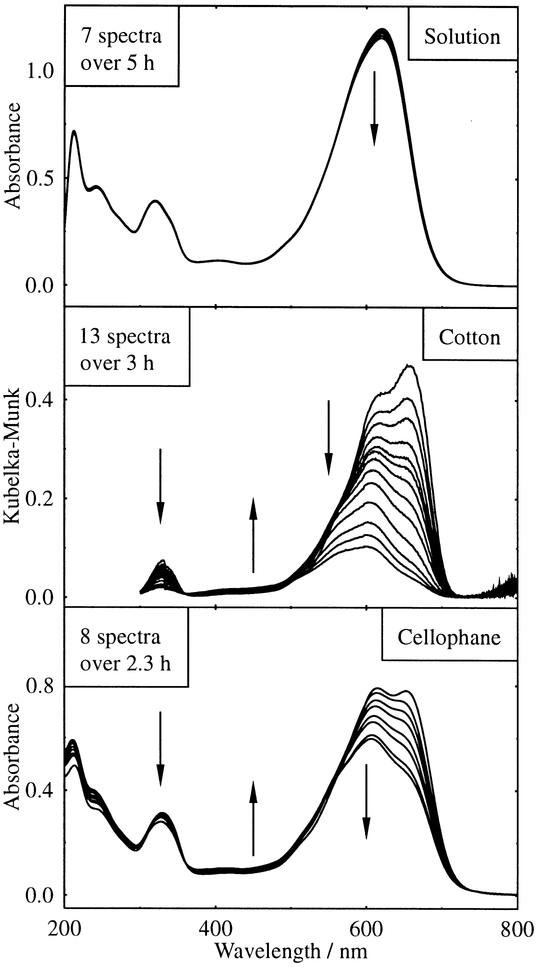


Fig. 5. UV–visible spectra of Direct Blue 1 in solution, on cotton, and in cellophane, recorded during 647.1-nm irradiation.

The UV–visible absorption spectra of Direct Blue 1 in cellophane, recorded during 2.3 h irradiation at 647.1 nm also show rapid fading. The absorption feature at 653 nm fades faster than the other main visible absorption band at 614 nm, and there is little change near 550 nm; there was also a slight colour change from blue to purple during the initial stages of photofading: these effects are similar to those observed for the cotton sample. The estimated quantum yield for fading of Direct Blue 1 in cellophane is $\phi_{\text{fade}}=7\times10^{-6}$, calculated from the changes over the first minute of irradiation.

4. Discussion

4.1. Steady-state spectra

The same general changes in the UV–visible spectrum of Acid Red 52 are observed on going from solution to either paper or cellophane. Higher concentrations of Acid Red 52 yield spectra with an additional band on the short-wavelength side of the visible absorption band, in all three environments, which may be attributed to an increase in the concentrations of dimer and higher aggregates, as reported for rhodamine 6G [8,9] and rhodamine B in aqueous solution [9]. If the association constants for Acid Red 52 are similar to those of these other dyes, then both dimers and higher aggregates will be present at the higher concentration used here to record the spectra presented in Fig. 2. The red-shift in the absorption maximum of Acid Red 52 observed on going from solution to paper or cellophane is clearly not due to aggregation because aggregation leads to a shift in absorbance to the blue: it may be attributed to a change in the energy of either the ground and/or the excited electronic state, probably arising from a small change in the structure of the dye on surface deposition; further studies will be required to determine the nature of this change.

The UV–visible spectra of Direct Blue 1 show similar changes to those of Acid Red 52 on going from solution to cotton, and these changes are replicated similarly on going from solution to cellophane. The additional absorption feature in the spectra of the cotton and cellophane samples of Direct Blue 1, at ca. 655 nm, does not arise from the aggregation process observed in solution because, again, aggregation in solution shows increased absorption on the short-wavelength side of the visible absorption band. The new absorption feature in the spectra of Direct Blue 1 on a surface may arise, like that of Acid Red 52, from a change in structure on deposition; again, further studies will be required to determine its nature.

4.2. Photofading studies

The photofading studies show that, for both Acid Red 52 and Direct Blue 1, fading in solution is very slow, with a low quantum yield, and that there is a significant increase in fading when the dye is deposited on to paper or into cotton. The increase in fading rate and increase in quantum yield are also observed when the dyes are incorporated into cellophane films. Each dye shows distinct spectral changes as it undergoes photofading on paper or cotton, and these spectral changes are replicated by the respective cellophane samples: Acid Red 52 shows the growth of a weak absorption feature at ca. 450 nm; Direct Blue 1 shows initial rapid fading of the absorption feature at ca. 655 nm. In addition, the large changes in the spectral profile on fading for Direct Blue 1 on a surface suggest that the fading process involves several steps. Similar studies of other ink dyes and cotton dyes, and further in-depth analyses of these data reveal further similarities between dye fading on paper or cotton and dye fading in cellophane; these more extensive studies reveal subtle aspects of the multi-step mechanisms involved in the photofading reactions and will be reported in full elsewhere.

5. Conclusions

Dye photofading in solution does not always mirror dye photofading on a surface. For more realistic studies of dye fading on a surface such as paper or cotton, dyes may be incorporated simply into cellophane films and their fading studied conveniently using conventional transmission spectroscopy. The resulting absorption spectra generally are better-defined than spectra recorded using diffuse reflectance techniques, they can be recorded over a larger wavelength range, and they are simpler to interpret. The photofading properties of dyes can be studied easily and quantitatively in cellophane, and very small changes can be followed readily.

The two structurally diverse dyes studied here showed different spectral changes when deposited onto a cellulosic surface from solution, and in each case the resulting sample showed decreased lightfastness. Both the spectral changes and the decreased lightfastness were mimicked when the dyes were incorporated into cellophane. These similarities show that cellophane can be used as a convenient mimic for studies of dye photofading in cellulosic media such as paper or cotton.

Acknowledgements

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