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The interaction of aliphatic amines with safranine T in aqueous solution

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Abstract

The photophysics of the excited states of safranine T and its reactions with aliphatic amines were studied in aqueous solution. The fluorescence lifetime of the singlet state was found to be 1.3 ns at 20 °C in water, and increases in non-hydroxylic solvents. This state is quenched by trialkylamines with nearly diffusional rate constants. In addition to the intense absorption of the monoprotonated form of the triplet state at 820 nm, a weaker absorption at 420 nm was detected. The non-protonated form also has a residual absorption at 820 nm. The lifetime of the non-protonated triplet was found to be around 15 μs. The monoprotonated triplet state of the dye is quenched by amines with rate constants of about 1×10^9 M^{-1} s^{-1}, too high to be ascribed to a charge transfer mechanism. Similar to the reaction in organic solvents, this reaction proceeds by a proton transfer mechanism, leading to the non-protonated form of the triplet state. This form is then quenched by another amine molecule to give the corresponding semireduced species.

Keywords: Safranine T; Aliphatic amines; Interaction; Absorption; Fluorescence

1. Introduction

The photoreduction of dyes by various types of electron donors has been studied quite often and, in many cases, mechanisms accounting for the observed results have been proposed and explained in terms of electron transfer theory [1,2]. In the specific case of xanthene dyes, few studies involving nitrogen compounds have been performed. Of these, in most cases, only the photoreduction by aromatic amines has been studied, generally in organic solvents. The photoreduction of methylene blue and thionine by anilines and anilinomethanesulphonates has been studied by Kayser and Young [3], Kikuchi et al. [4], Steiner et al. [5] and Neumann et al. [6], and the results were interpreted using the Rehm and Weller relationship [1]. The photoreduction of safranine by anilines [7] and anilinomethanesulphonates [8] has also been studied by Neumann et al. Timpe and Neuenfeld [9] studied the photoreduction of several dyes by triethanolamine within the scope of photoinitiated polymerizations. The only study of the photoreduction of a xanthene dye by aliphatic amines in aqueous solution was reported by Kayser and Young [10] using methylene blue. The lack of data may possibly be due to the fact that these reactions seem to be irreversible and lead efficiently to the photobleaching of the dye. Photobleaching by amines has also been described for other dyes [11].

The interest in these reactions has grown significantly in recent years due to the use of xanthene dyes in photoinitiated polymerization reactions. In these systems, which include a dye, an amine and a monomer, the initiation process is started by an amine-centred free radical formed during the photoreduction of the excited dye [12]. Recently, Timpe and coworkers [13,14] have reported the quenching of safranine by aliphatic amines in methanol in order to ascertain their efficiency in photoinitiated polymerization. We also studied the interaction of amines of this type with the excited states of safranine in methanol and acetonitrile [15], and found that the deactivation of the initially formed triplet state proceeded by a proton transfer process. A knowledge of the reaction mechanisms involving the excited states of dyes used as photoinitiators is of great importance in order to understand the processes occurring at the early stages of photoinitiated polymerization [16,17].

In recent years, considerable effort has been devoted to the study of water-soluble photoinitiator systems [12,18–21]. Although xanthene and acridine dyes have been used as photoinitiating systems for polymerization in the presence of reducing agents in aqueous solution [12,18], these studies have dealt mainly with the kinetics of polymerization,

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whereas the photochemical mechanism has received less attention. Therefore, in this paper, we report the interaction of excited safranine T with some aliphatic amines used in photoinitiation formulations.

2. Experimental details

Safranine T chloride (Merck) was recrystallized from ethanol before use. Triethylamine (TEA, Aldrich) and triethanolamine (TEOHA, Aldrich) were purified by vacuum distillation before use.

Fluorescence steady state measurements were performed on a Fluorolog Spex fluorometer. Transient absorption spectra and transient decays were measured on an Applied Photophysics laser kinetics spectrometer. Excitation at 532 nm was performed using the second harmonic of an Nd-YAG laser (Spectron). Safranine solutions in water (1×10^{-5} M) were deoxygenated by nitrogen bubbling.

Fluorescence decays were measured with a single-photon timing technique using a CD-900 Edinburgh Instruments spectrometer operating with a low-pressure nanosecond H_2 flash lamp at a pulse frequency of 25 kHz. All fluorescence measurements were performed with samples at 20 °C in air-equilibrated conditions. Exponential fitting of the fluorescence decays was performed using a non-linear least-squares iterative routine based on the Marquardt algorithm. The software for data analysis was supplied by Edinburgh Instruments.

3. Results and discussion

The fluorescence decays of safranine T were monoexponential with lifetimes in the range 1.3–3.6 ns depending on the solvent. Fig. 1 illustrates the change in the fluorescence decay rate of the dye in acetone–water mixtures and Table 1 shows the lifetimes in pure solvents as well as mixtures. Guha et al. [22] reported lifetimes of 1.15 and 2.88 ns for safranine T in water and sodium dodecylsulphate (SDS) micelles respectively. A comparison with the present results is not possible as the temperature of the measurements was not mentioned in their work.

The lifetimes in Table 1 suggest that the effect of the solvent on the deactivation of the singlet excited state of SfH^+ depends on its protic character rather than its polarity.

The transient absorption spectrum of safranine in neutral aqueous solution in the absence of amine is shown in Fig. 2 Two main peaks can be observed, one around 820 nm and the other at 420 nm. These peaks are assigned to the monoprotonated triplet state of the dye $^3SfH^+$. It is well established that this species absorbs at 820 nm in organic solvents [16,23]. The absorption at 420 nm has only recently been reported in organic solvents [15]. In an earlier study of safranine in water, Baumgartner et al. [24] observed similar behaviour in the 600–800 nm region, but failed to observe any absorption of this species below 450 nm. Furthermore, Gopidas and Kamat [25] reported a transient absorption at 410 nm for the similar dye phenosafranine. Decays measured at 420 and 830 nm follow identical first-order kinetics with lifetimes around 50 μs, confirming that the absorption in the 420 nm region also corresponds to the monoprotonated triplet.

In sufficiently basic solutions, the transient spectrum changes, showing a strong band around 420 nm and a weaker absorption at 830 nm (see Fig. 2). Although the first band, attributed to the deprotonated triplet species of the dye, has been observed [24], the latter has not been reported previously. The lifetime of this transient of safranine measured at 420 and 830 nm is around 15 μs. Thus the decay rate constant for the species present in this condition can be calculated as 6×10^4 s^{-1}, and is somewhat larger than that reported by Baumgartner et al. [24] (1.7×10^4 s^{-1}). However, the experimental set-up used in Ref. [24] only allowed measurements starting about 50 μs after excitation.

3.1. Interaction with amine

The steady state fluorescence quenching of safranine by TEOHA and TEA was measured in pure water. Since the rate of this process is pH dependent, all measurements were carried out at pH 10. The Stern–Volmer plots were linear and presented slopes of 11 and 12 M^{-1} respectively. Using the lifetime determined for singlet safranine in water, 1.34 ns, the quenching rate constants can be evaluated as 8.2×10^9 and 8.9×10^9 M^{-1} s^{-1}. These values can be considered to be within the diffusional limit. The quenching reaction can be assumed to proceed by a charge transfer mechanism, as previously proposed [15] for the same systems in organic solvents. An exciplex intermediate has also been postulated for the quenching of the singlet states of other dyes by several amines [2a,23,26,27].

The addition of low concentrations of amines ([TEA] < 0.05 mM or [TEOHA] < 0.5 mM) to neutral aqueous solutions of safranine resulted in a gradual decrease in the lifetimes of the transients at 830 and 420 nm. The addition of larger quantities caused only a slight effect on the decay time. The dependence of the lifetime on the concentration of TEA is shown in Fig. 3(a). A plot of the inverse of the lifetime as a function of TEA at low concentrations of the amine is shown in Fig. 4. A straight line can be drawn through the experimental points, corresponding to a quenching rate constant of 1.23×10^9 M^{-1} s^{-1}. A very similar value is calculated from the variation of the lifetimes obtained from the decays at 420 nm. On the other hand, the observed quenching of the initial decay of the signal at 420 nm can be evaluated to have a rate constant of about 1×10^9 M^{-1} s^{-1}, confirming that the analysed signal corresponds to the $^3SfH^+$ form of the triplet. As for similar reactions in organic solvents [15], this value is too high for electron transfer quenching, so that the reaction responsible for the disappearance of the protonated triplet could be proton transfer, i.e.

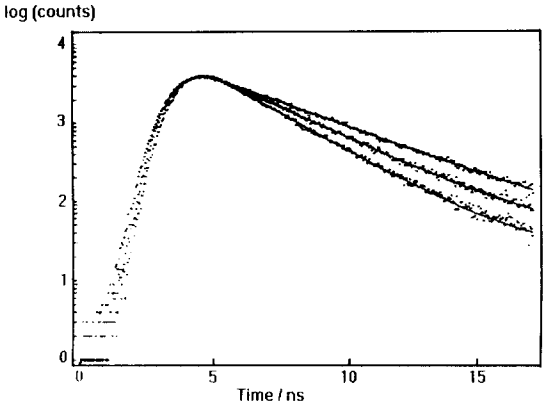


Fig. 1. Fluorescence decays of safranine T in acetone–water mixtures. From top to bottom: pure acetone, water–acetone 1:2 and 2:1 (for lifetimes, see Table 1).

Table 1
Safranine T excited singlet state lifetimes in different solvents at 20 °C

Solvent	τ (ns)	χ^2	ϵ
Acetonitrile	3.61 ± 0.02	1.14	37
Acetone	3.38 ± 0.01	1.15	21
Methanol	2.49 ± 0.02	1.06	33
Water	1.34 ± 0.02	1.05	80
Water–acetone (2:1)	2.12 ± 0.01	1.09	–
Water–acetone (1:2)	2.64 ± 0.01	1.20	–

ϵ is the dielectric constant of the solvent.

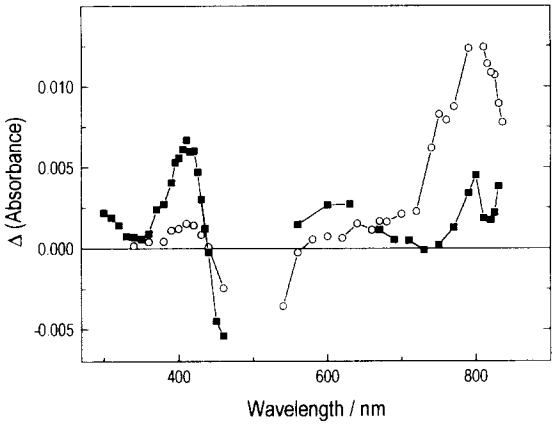


Fig. 2. Transient spectra of safranine (1×10^{-5} M) taken 4 μs after excitation (○) and in the presence of TEA (0.19 mM) 2 μs after excitation (■).

$$^3SfH^+ + R_3\ddot{N} \longrightarrow {}^3Sf + R_3\overset{+}{N}H \quad (1)$$

At sufficiently high concentrations of amine, the lifetimes of the transient absorptions at 830 and 420 nm fall to a limiting value of around 17 μs, similar to that found for the triplet of safranine in mineral basic solution, and thus corresponding to the non-protonated triplet ^3Sf (Fig. 3(a)).

The behaviour of the initial optical density at 830 nm, for different concentrations of amine in solution, is shown in Fig. 3(b). The addition of sufficient amine lowers the initial optical density to a non-zero constant value. This residual absorption corresponds to the non-protonated triplet, which also absorbs at this wavelength. The behaviour of OD_{830} can be estimated from

$$OD_{830} = \epsilon_P \times \left(\frac{[^3SfH^+]}{1 + K_{SV}[am]} \right) + \epsilon_D [^3Sf] \quad (2)$$

where ϵ_P and ϵ_D are the extinction coefficients of the protonated and deprotonated forms of the dye, K_{SV} is the Stern–Volmer constant for the quenching of the singlet state of the dye by the amine and [am] is the concentration of free amine. The extinction coefficient for the deprotonated form of the dye can be considered to be about 15% of that of the monoprotonated triplet (see Fig. 3(b)). Eq. (2) may be reordered to give

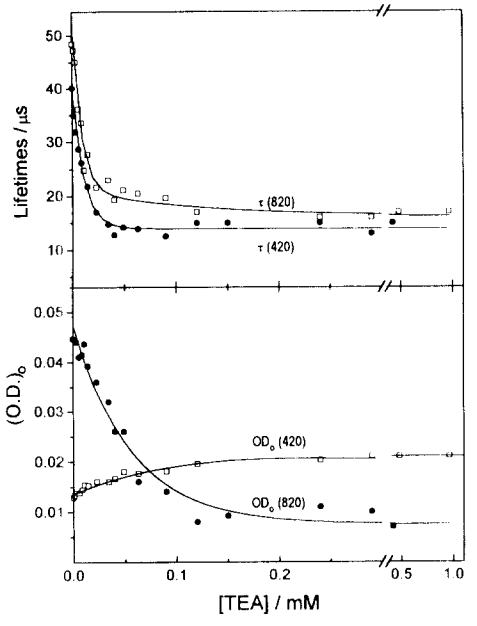


Fig. 3. (a) Lifetimes of the transient absorption of safranine in the presence of TEA measured at 830 and 420 nm. (b) Initial optical density of the safranine transient absorption at 830 and 420 nm.

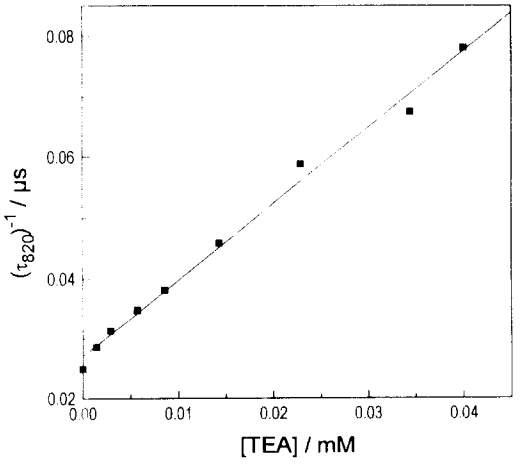


Fig. 4. Lifetimes of the transient absorption of safranine at 830 nm in the presence of low concentrations of TEA.

$$OD_{830}/\epsilon_P = \left(\frac{[^3SfH^+]}{1+K_{SV}[am]}\right) + 0.15 \times [^3Sf] \quad (3)$$

For TEA, K_{SV} is equal to 11 M^{-1} and the concentrations of both forms of the triplet dye can be calculated from the ground state equilibrium using 11.5 for the pK_a value of the dye [28] and 3.2 for the pK_b value of the amine.

$$SfH^+ + R_3N \rightleftharpoons Sf + R_3NH^+ \quad (4)$$

A comparison of the experimental values of the initial optical density and those calculated using Eq. (3) (normalized to unit OD/ϵ) is shown in Fig. 5.

In contrast with the absorption at 830 nm, the initial optical density at 420 nm increases on addition of amine, levelling off at TEA = 0.1 mM or TEOHA = 1 mM (Fig. 3(b)). In general, the behaviour of the system containing TEOHA is similar to that with TEA, as can be seen in Fig. 6, except for the effects of the different basicities of the amines. As larger amounts of amine are added to the solution, the acid–base equilibrium will tend to form more non-protonated safranine, so that less monoprotonated dye is present in the ground state,

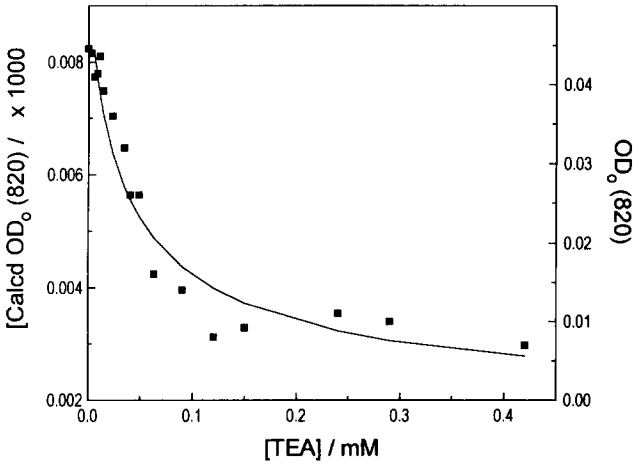


Fig. 5. Initial optical density of the transient absorption of safranine at 830 nm. Experimental data (■) and line calculated using Eq. (3).

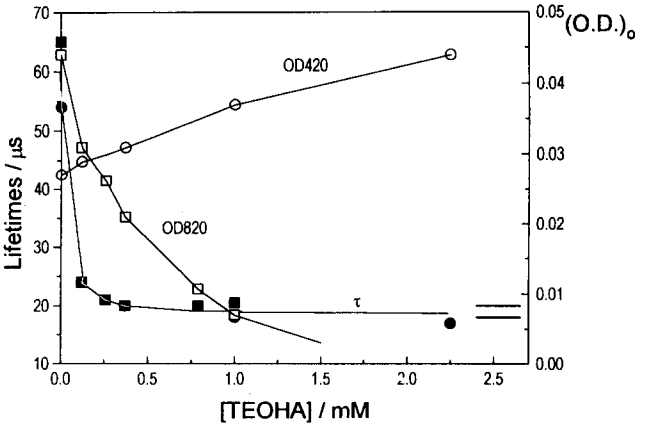
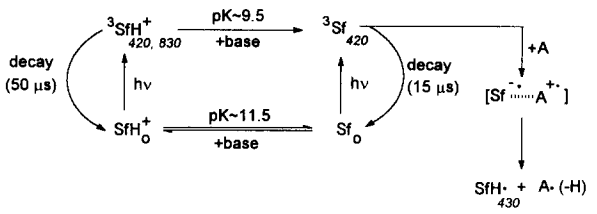


Fig. 6. Lifetimes and initial optical densities of the transient absorptions of safranine in the presence of triethanolamine.



Scheme 1.

and more non-protonated dye will be excited directly as shown in Scheme 1 (see Section 4).

At high amine concentrations, the decay of the 420 nm absorption is rather complex. It presents an initial fast component and a residual long-lived component (see Fig. 7). This remaining intensity is proportional to the amount of added amine. These results are consistent with the quenching of the non-protonated form of triplet safranine to give the corresponding semireduced form of the dye, which rapidly abstracts a hydrogen from the amine within the solvent cage, forming the SfH$^\bullet$ species which also absorbs in the 420 nm region [24].

$$^3Sf + R_3N \longrightarrow [Sf^- + R_3N^{\bullet+}] \longrightarrow SfH^\bullet + R_3\dot{N}(-H^+) \quad (5)$$

The long-lived component decays by second-order kinetics in the millisecond domain. Assuming that the rate constant for this decay is diffusional and that the concentration of the semireduced species is about 10^{-6} M, the lifetime of the species would be at least a couple of hundred microseconds. A plot of the long time absorption at 420 nm as a function of the amine concentration is presented in Fig. 8. This absorption will correspond to the semireduced form of the dye, as can be seen from the change in the transient absorption in this region when compared with the spectra taken 2 and 80 μs after excitation (inset in Fig. 8). It can be seen that, for TEOHA, the production of the radical is higher than for TEA at high concentration, but the curve for the latter grows faster. This is due to the higher basicity of TEA which produces a higher amount of initial ^{3}Sf at low concentration. When the

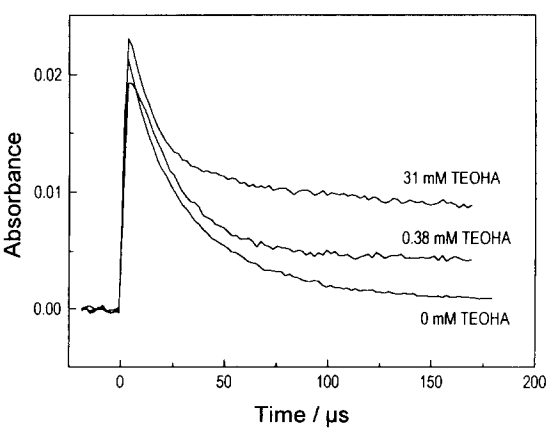


Fig. 7. Decays of the 430 nm transient absorption of safranine in the presence of increasing concentrations of triethanolamine.

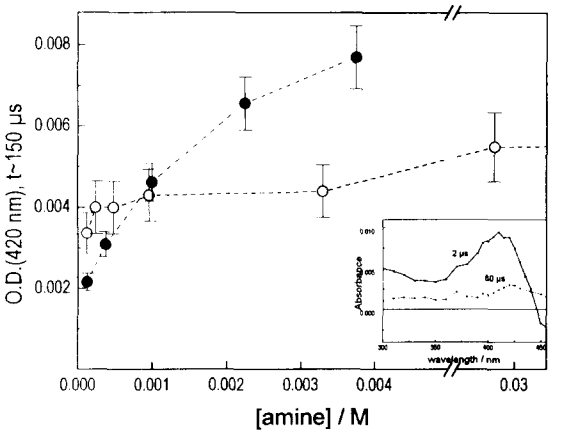


Fig. 8. Long-lived absorption (150 μs) at 420 nm as a function of TEA (○) and TEOHA (●) concentration. Inset: transient absorption of safranine (2×10^{-5} M) in the presence of TEA (0.19 mM) 2 and 80 μs after irradiation.

amine concentration is such that similar amounts of non-protonated triplet are produced in the fast initial step, TEOHA production of the radical becomes predominant due to the higher efficiency of this amine in electron transfer quenching, as previously observed in the non-diffusional singlet quenching of safranine in organic solvents [15]. This high radical yield is also in agreement with the high efficiency observed for the system safranine–TEOHA in the photoinitiation of vinyl polymerization [17].

4. Conclusions

The interaction between trialkylamines and the excited states of safranine in aqueous solution occurs by a charge transfer mechanism in the singlet state. At relatively low concentration of the amines, the interaction is with the mono-protonated form of the triplet state, involving proton transfer quenching. At higher concentrations, the non-protonated state is present, which decays faster than the monoprotonated transient. The quenching of this state is slow, requires high amine concentrations, such as those used in photoinitiated polymerization, and leads to the semireduced form of the dye.

Although the main absorption peaks of the monoprotonated triplet and non-protonated triplet are always found at 820 and 420 nm respectively, significant absorbances (about 15%) were detected for these species at 420 and 830 nm. The decay rate constant of the non-protonated triplet was determined to be 6×10^{4} s^{-1}.

The mechanism explaining the behaviour of the dye in the presence of increasing amounts of amine is shown in Scheme 1.

Acknowledgements

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