Journal of Photochemistry and Photobiology A: Chemistry 226 (2011) 51–56

Contents lists available at SciVerse ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Photophysics of safranine-O and phenosafranine in reverse micelles of BHDC

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ARTICLE INFO

Article history:
Received 30 June 2011
Received in revised form 18 August 2011
Accepted 12 October 2011
Available online 19 October 2011

Keywords:
Safranine
Phenosafranine
Photophysics
Triplet state
Reverse micelles

ABSTRACT

The photophysics of safranine-O (3,7-diamino-2,8-dimethyl-5 phenyl phenazinium chloride, SF) and phenosafranine (3,7-diamino-5-phenyl phenazinium chloride, PSF) was investigated in reverse micelles (RMs) of the cationic surfactant benzyl hexadecyl dimethylammonium chloride (BHDC). The excited singlet state properties were measured by absorption and fluorescence spectroscopy. All the measurements indicate that both dyes are localized in the interface, sensing a medium of lower polarity than water. Stokes' shift increases and fluorescence quantum yield decreases with increasing the water content, but never reach the values or pure water. The triplet state properties of the dyes in RMs were investigated by laser flash photolysis. The maximum of the T–T absorption spectra in RMs confirms that, in spite of their positive charge, the dyes remain at the interface co-micellizing with BHDC. The triplet lifetime is much longer in the RMs than in homogeneous organic solvents. The two dyes present a different dependence of their photophysical properties with the water content. The two methyl groups in the ring of SF produce a stronger preference of the dye for a hydrophobic environment, and consequently a deeper location in the interface closer to the organic phase. A remarkable difference is observed in the triplet quenching by aliphatic amines. While the quenching by hydrophobic tributylamine is much lower in BHDC/benzene RMs than in a homogeneous solvent, the hydro soluble triethanolamine is near two orders of magnitude more effective in the RMs than in homogeneous solution. This is explained by the different local concentration of the amines in the interface.

1. Introduction

Reverse micelles (RMs) and microemulsions have attracted considerable interest in recent years because they can provide "nano-sized reactors" for chemical, photochemical and biological reactions [1]. In reverse micelles a solute can be located in a variety of microenvironments. The simplest approach is to consider the system as composed by two pseudophases: the bulk solvent and the microaggregates formed by the surfactant molecules and the entrapped water. However, a three pseudophases model is more often preferred, comprising the bulk solvent, the surfactant–water interface and the water pool. Moreover, four different probable locations for a small molecular probe in a reverse micelle have been proposed. In this model two interfacial regions are distinguished, the bulk solvent/micelle interface and the interior surfactant/water pool interface [2]. The three governing factors for solubilization are electrostatic, hydrophobic, and specific interactions of the RM interface with the solubilized molecules. The localization of the solute will depend also on the water/surfactant ratio since several interface properties, such as microviscosity and micropolarity, are influenced by this parameter [3]. In many cases a dye molecule was used as a probe to characterize reverse micelles and to investigate the effect of the surfactant and dye molecular structure on its localization in the microheterogeneous system [4,5].

Most of the photophysical and photochemical studies in reverse micellar systems have been carried out using the anionic surfactant Aerosol OT (AOT, sodium bis (2-ethylhexyl) sulfosuccinate) [2]. This surfactant forms reverse micelles in a variety of organic solvents and is able to support high water contents, up to $w = 50$ ($w = [H_2O]/[\text{surfactant}]$). On the other hand, cationic surfactants have been much less explored. In particular, benzyl hexadecyl dimethylammonium chloride (BHDC) is the most employed cationic surfactant for RMs and microemulsion studies [4(a),6]. In this case the positive interface offers a different microenvironment and consequently diverse properties of the solubilized substrate. BHDC reverse micelles are less stable than those of AOT and the range of w is limited to w <25–30 depending on the organic solvent. It has been shown that truly reverse micelles are formed at BHDC concentrations higher that 0.02 M in benzene [7]. It was also shown that in these systems, hydrophobic and electrostatic effects of the interface can control the course of a photochemical reaction [8].

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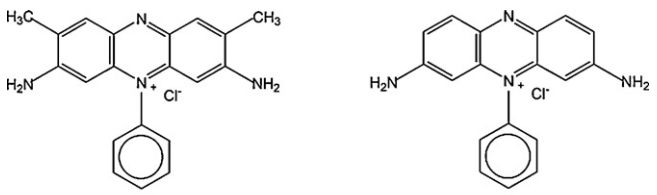
doi:10.1016/j.jphotochem.2011.10.014



Scheme 1.

We have previously investigated several photoinitiating systems for vinyl polymerization operating in the visible region based on synthetic dyes [9,10]. In particular the phenazinium dye safranine-O (3,7-diamino-2,8-dimethyl-5-phenylphenazinium chloride, SF), which absorbs around 500 nm, was used as sensitizer and several aliphatic amines were employed as co-initiators (hydrogen donors) [9]. This system was found to be highly efficient for the free radical polymerization of vinyl monomers and it was also shown to be useful for photopolymerization in aqueous media [11]. The addition of a third component (diphenyliodonium salt) improved the efficiency of the system SF–triethanolamine in aqueous photopolymerization of acrylamide [12]. The deactivation mechanism of the excited states of SF, and the related dye phenosafranine (3,7-diamino-5-phenyl phenazinium chloride, PSF), in the presence of aliphatic and aromatic amines have been the subject of several studies of our group [13–16]. Therefore, it was of interest to explore the possibility of using these photoinitiator systems in reverse micelles. To this end we have undertaken an investigation of the photophysical properties of SF and PSF in reverse micelles of BHDC. These two dyes differ in terms of methyl substitution on the planar phenazinium skeleton (Scheme 1). Differential extent of hydrophobicity due to the presence of methyl substitution may cause a different location of the dyes in the reverse micellar system, and in turn different photophysical behaviour. SF was widely employed to characterize normal micelles [17], to investigate the kinetics of electron transfer reactions in these media [18] and in studies DNA–dye interactions [19]. On the other hand, similar studies employing PSF are very much scarce. In RMs absorption and fluorescence emission spectra of SF were determined in order to understand the localization of the dye in the microheterogeneous domains and to determine the properties of the microenvironment where the dye is located. Most of these studies were carried out in AOT–heptane solutions. Since the interfacial region is composed by the negative heads of the surfactant, it is expected that the positive dye will remain either close to the hydrated heads or oriented toward the bulk organic phase. From fluorescence studies Bose et al. [5] suggested, that at low *w* values SF does not penetrate into the reverse micellar core, rather it binds at the interfacial region. These authors also compare the photophysics of SF and PSF in AOT RMs. The fluorescence quenching of SF by AgCl nanoparticles has been investigated in the W/O microemulsion medium at different $[H_2O]/[AOT]$ ratios by Pramanik et al. [20]. The fluorescence quenching of SF by the inorganic ions Fe^{2+}, $[Fe(CN)_6]^{3-}$ and Cu^{2+} was studied in AOT RMs and microemulsions in various non-polar solvents [21]. Chaudhuri et al. [22] studied the luminescence behaviour of PSF in RMs of AOT in heptane. They concluded that the photophysical properties of the dye do not reach those in pure water even at high w.

All these studies of the photophysics of SF and PFS in RMs have been based on the absorption and fluorescence emission spectra and lifetime measurements. The effect of organized media on the triplet state of these dyes has received much less attention. The effect of microheterogeneous media, polyelectrolytes and normal SDS micelles, on the triplet state of the dye was investigated by Pastre and Neumann [23]. To our knowledge the triplet state properties of these dyes in RMs have not yet been reported. Since most of the applications of SF and PSF involve the triplet state and its electron transfer reactions with electron donors, it is of interest to study these processes in RMs.

2. Material and methods

2.1. Materials

Safranine-O and phenosafranine from Aldrich (≥85%) were recrystallized from ethanol. BHDC was two times recrystallized from ethylacetate and dried under vacuum. Benzene and methanol were from Sintorgan (HPLC grade) and used as received. Water was purified through a Millipore Milli-Q system. Reverse micelles solutions were prepared by the addition of a small amount of the dyes dissolved in water to a 0.05 M BHDC/benzene solution. The water:micelle content, $w = [H_2O]/[\text{surfactant}]$, was varied by adding neutral water. The final analytical concentration of the dye was *ca.* 5×10^{-6} M. Since the aggregation number of BHDC in benzene at $w = 15$ is *ca.* 500 [24], at the surfactant concentration used the mean occupation number of the dye was less than 0.05. The aliphatic amines triethanolamine (TEOA) and tributylamine (TBA) were commercially available and were purified by standard procedures when necessary.

2.2. Measurements

Absorption spectra were obtained by using a Hewlett Packard 6453E diode array spectrophotometer. Fluorescence spectra were measured with a Spex Fluoromax spectrofluorometer in air equilibrated solutions. Fluorescence lifetimes were determined by using the time-correlated-single-photon-counting technique with a FL 900 Edinburgh Instruments equipped with a PicoQuant subnanosecond pulsed LED emitting at 495 nm. Fluorescence quantum yields were determined relative to those of the dyes in MeOH [25,26]. Transient absorption measurements were carried out by excitation at 532 nm using a laser flash photolysis equipment as previously described [27]. The samples were deoxygenated by continuous bubbling with high purity argon. All measurements were carried out at 30 °C.

3. Results and discussion

3.1. Singlet state properties

Absorption and fluorescence spectra of SF and PSF are highly dependent on the polarity of the solvent [25,26]. In water solutions, SF shows absorption and emission maxima centred at ~520 nm and ~586 nm, respectively. A red shift in the ground-state absorption and a blue shift in the emission band of both dyes are observed when the solvent polarity decreases. In BHDC reverse micelles the spectral characteristics depend on the water content. The absorption spectra are more sensitive to the value of *w* than the fluorescence emission spectra. The absorption maximum of safranine is blue shifted from 548 nm at $w = 2$ to 539 nm at $w = 20$. On the other hand, the fluorescence emission spectrum remains unchanged in position ($\lambda_{max} = 572$ nm) but decreases in intensity as shown in Fig. 1.

It is to be noticed that in homogeneous solvent the absorption maxima for SF are at 529 nm in MeOH and 537 nm in 2-propanol [25]. The fluorescence emission maxima are at 564 and 562 nm in MeOH and 2-propanol, respectively. Similarly, for PSF the emission changes only 2 nm on going from $w = 2$ to $w = 20$ while in the same interval the absorption changes by more than 12 nm. Fluorescence lifetime and quantum yields of the dyes present a small

Table 1
Absorption and fluorescence parameters in BHDC/benzene reverse micelles.

Medium	w	Safranine				Phenosafranine			
		λ_{max}(abs)/nm	λ_{max}(em)/nm	τ_F/ns[b]	Φ_F[c]	λ_{max}(abs)/nm	λ_{max}(em)/nm	τ_F/ns[b]	Φ_F
BHDC[a]	2	547.5	572	1.73	0.17	546.5	571	1.55	0.12
	5	543.5	572	1.74	0.15	541.5	573	1.38	0.11
	7	541.5	572	–	0.15	539.5	574	1.31	0.11
	10	540	572	1.70	0.15	538	574	1.25	0.10
	15	539.5	572	1.67	0.14	536	574	1.21	0.09
	20	539	572	1.66	0.14	534	574	1.20	0.09
MeOH		529	568	2.60	0.21	527	567	2.10	0.20

[a] BHDC concentration 0.05 M.
[b] Estimated error ±2% or ±0.02 ns, whichever the greater.
[c] Estimated error ±10%.

Table 2
Absorption maximum (λ_{max}), absorption coefficient (ε), lifetime (τ) and quantum yield (Φ_T) of the triplet state of safranine-O and phenosafranine in homogeneous and BHDC/benzene reverse micelle media.[a]

Medium	Safranine-O			Phenosafranine		
	λ_{max}/nm (ε/M^{-1} cm^{-1})	τ/μs	Φ_T	λ_{max}/nm (ε/M^{-1} cm^{-1})	τ/μs	Φ_T
Water	720 (7600), 805 (16,200)	60 ± 5	0.28	704 (9400), 785 (15,800)	55 ± 5	0.19
MeOH	730 (7300), 822 (19,500)	18 ± 2	0.31	715 (9550), 800 (21,000)	15 ± 2	0.28
BHDCw = 15	750 (12,700), 850 (28,000)	106 ± 5	0.27	730 (11,500), 810 (22,000)	107 ± 5	0.20

[a] Estimated errors in absorption coefficients and triplet quantum yield are ±20%.

dependence with the water content. The singlet state properties of both dyes in BHDC are collected in Table 1. They are independent of BHDC concentration in the range 0.05–0.1 M. Also in the table are shown the values in methanol for the sake of comparison. This solvent was chosen because in it the photophysical properties of both dyes were determined under similar experimental conditions. Moreover, it offers an intermediate polarity between the organic phase and the water pool. It can be seen that fluorescence lifetimes are shorter and quantum yields are lower in the RMs than in the alcohol. Since these two quantities increase when the polarity of the solvent decreases, it could be concluded that both dyes are sensing a medium of micropolarity higher than that of MeOH, but lower than pure water where the fluorescence lifetime and quantum yield of SF are 1.3 ns and 0.058, respectively. Nevertheless, the Stokes' shift in BHDC at high w is slightly lower than in MeOH, and this is an indication of a lower polarity of the medium. This points to the risk of extracting conclusions about the micropolarity of an organized medium based on only one or two photophysical parameters. The Stokes' shift and fluorescence quantum yield (Φ_F) of SF and PSF as a function of the water content of the reverse micelles are shown in Fig. 2. The Stokes' shift increases reaching a plateau of 1080 cm^{-1} at w = 10 for SF while it is 1300 cm^{-1} and still increasing at w = 20 in the case of PSF. At the same time Φ_F decreases to 0.14 for SF and 0.095 for PSF. A stronger dependence with the water content is clear in the case of PSF. The values of the Stokes' shift and Φ_F are to be compared with those in pure water, 2233 cm^{-1} and 0.058 respectively for SF, and 2274 cm^{-1} and 0.04 for PSF. The important conclusion from these observations is that both dyes, in spite of bearing a positive charge and the possible electrostatic repulsion from the interface, are not localized in the centre of the water pool, and the most probable site for both dyes is co-micellizing in the positive interface of the RMs.

When the two dyes are compared it is apparent a different dependence of the photophysical properties with the water content. Thus, for PSF the Stokes' shift increases monotonically with the water content and its lifetime is only 1.20 ns at w = 20. This may

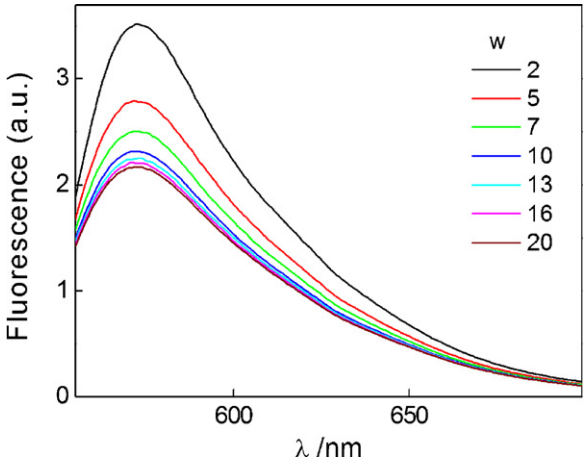


Fig. 1. Fluorescence spectra of safranine-O in BHDC reverse micelles as a function of the water content. [BHDC] = 0.05 M.

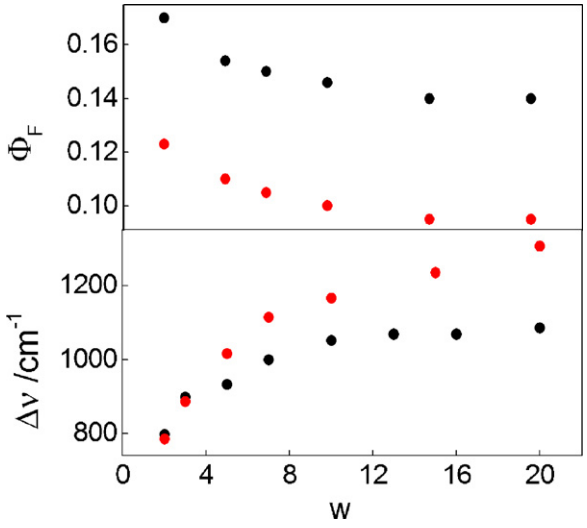


Fig. 2. Fluorescence quantum yield and Stokes' shift ($\Delta\nu$) for safranine-O (black) and phenosafranine (red) in BHDC 0.05 M/benzene reverse micelles as a function of the water content. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

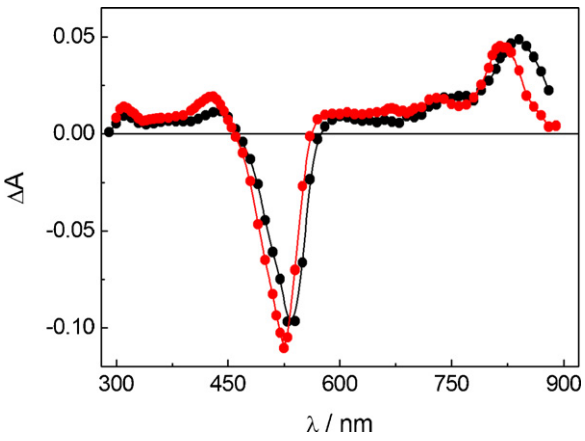


Fig. 3. Transient absorption spectrum of safranine-O immediately after the laser pulse at 532 nm in MeOH (red) and in BHDC reverse micellar solution (black). [BHDC] = 0.05 M, w = 15. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

be taken as an indication of a more aqueous environment for this dye than for SF. The two methyl groups in the ring of the latter makes a stronger preference of the dye for a hydrophobic environment. Therefore, it will be deeper in the interface and closer to the organic phase.

3.2. Triplet state properties

The T–T transient absorption of SF in MeOH presents three main bands at 430, 735 and 820 nm, Fig. 3. It decays in tens of microseconds, mainly by self-quenching, to the semireduced and semioxidized forms of the dye [14]. In the reverse micellar system the lower energy bands are red shifted to 750 and 850 nm (Table 2).

The transient absorption spectrum of PSF in BHDC can be seen in Fig. 4. The main bands in BHDC are at 810, 730 and 430 nm while in MeOH they are at 800, 710 and 430 nm. In the inset of Fig. 4, the initial absorption spectrum (2 μs) is compared with the long time spectrum (150 μs) normalized at the maximum at 810 nm. It can be seen that the absorption in the region 400–450 nm is relatively much higher in the spectrum at 150 μs. That region corresponds to the absorption of the semireduced and semioxidized forms of the dye [14]. In homogeneous solvents both species originate in an electron transfer self-quenching reaction. Since the mean

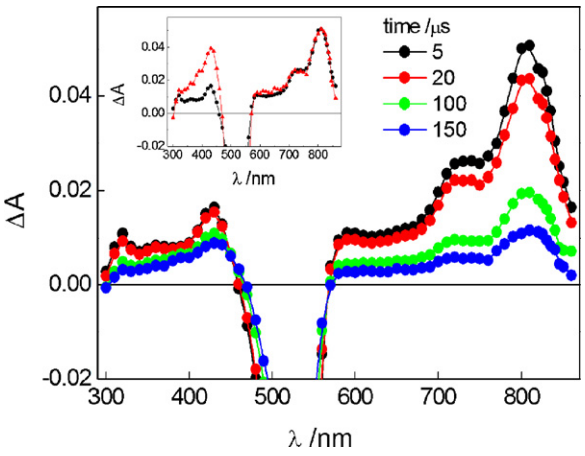


Fig. 4. Transient absorption of PFS in BHDC 0.05 M, w = 15. Inset: Spectrum at 2 μs (black) and 150 μs (red) normalized at the maximum (810 nm). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Table 3
Singlet quenching rate constants (in units of 10^9 M^{-1} s^{-1}) in methanol [14,16] and BHDC 0.05 M, w = 15.

	TEOA		TBA	
	MeOH	BHDC	MeOH	BHDC
Safranine	4.1 ± 0.1	16.0 ± 0.5	2.8 ± 0.1	No quenching
Phenosafranine	2.1 ± 0.1	29.5 ± 1	1.5 ± 0.05	No quenching

occupation number of the RMs by the dye is less than 0.05 it is most unlikely that a self quenching process takes place within a given RM. Therefore, the origin of the long time absorption may be found in either a reaction of the triplet with the surfactant, or with an impurity not detected, or more likely, by self quenching by ground state molecules of the dye in an exchange mechanism between RMs with a time constant of several tens of microseconds.

It can also be noted that the T–T absorption bands of PSF in the red zone of the spectrum are shifted to the blue with respect to those of SF. This is a result of the different ring substitution of the dyes, since a similar effect is observed in homogeneous solvents [28].

3.3. Excited states quenching by aliphatic amines

The quenching of singlet and triplet excited states by aliphatic amines was investigated. Two amines were chosen, TEOA a water soluble amine that will be located in the water pool of the RMs, and TBA, a hydrophobic molecule that will reside in the bulk organic solvent.

The kinetics of the singlet quenching was determined by fluorescence lifetime measurements in the absence and the presence of the amines. The fluorescence decay could be fitted to a monoexponential kinetics in all cases. Apparent quenching rate constants were determined according to Eq. (1):

$$\tau^{-1} = \tau_o^{-1} + {}^1k_q[\mathrm{Q}] \quad (1)$$

where τ_o and τ stand for the fluorescence lifetime in the absence and the presence of the quencher Q, respectively. Rate constants ${}^1k_q$ in BHDC, expressed in terms of the analytical concentrations of the amine, are collected in Table 3 together with those in MeOH for the sake of comparison.

It was previously demonstrated that singlet quenching of SF by aliphatic amines takes place by an electron transfer mechanism [14]. Since TEOA and TBA have similar oxidation potentials, similar quenching rate constants are expected and this is in fact observed in homogeneous solvents as can be seen in Table 3. On the other hand in BHDC the scenario is totally different. While TEOA is more efficient in the RMs by *ca.* one order of magnitude, TBA does not quench the fluorescence of the dyes. Moreover, in MeOH the rate constant for the quenching of SF is twice that for the quenching of PSF and this situation is reverse in BHDC. The values of the apparent rate constants for the quenching by TEOA are higher than the values in MeOH, and in the case of PSF for more than one order of magnitude. They are even higher than the diffusional limit, 1.2×10^{10} M^{-1} s^{-1} in MeOH [29]. This result is a consequence of the high occupation number of TEOA (analytical concentration in the 0.005–0.015 M range) and its preferential location in the interfacial region. The lack of quenching by TBA may be understood by a restricted access of the amine to the interfacial region that precludes the interception of the short lived singlet state. The higher value for the quenching of PSF by TEOA compared with SF reflects the different location of the dyes. The former, as discussed above, senses a more aqueous medium where the hydrophilic TEOA is preferentially located. This is further confirmed by the triplet state quenching.

The triplet state of both dyes is efficiently quenched by aliphatic amines in homogeneous and microheterogeneous systems and it

Table 4
Triplet quenching rate constants (in units of 10^7 M^{-1} s^{-1}) in methanol [14,16] and BHDC 0.05 M, $w = 15$.

	TEOA		TBA	
	MeOH	BHDC	MeOH[a]	BHDC
Safranine-O	1.3 ± 0.2	45.0 ± 2	24 ± 1	0.19 ± 0.2[a]
Phenosafranine	2.0 ± 0.2	86.0 ± 2	46 ± 2	0.18 ± 0.05[b]

[a] From initial slopes.
[b] Linear plot.

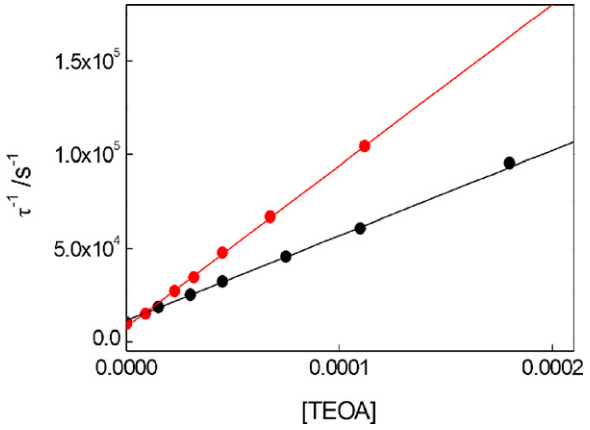


Fig. 5. Triplet quenching by TEOA of SF (black) and PSF (red) in BHDC 0.05 M, $w = 15$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

decays with a first order kinetics. Apparent triplet quenching rate constants were obtained from lifetime measurements carried out by laser flash photolysis and are collected in Table 4. In Figs. 5 and 6 plots of the reciprocal of the triplet lifetimes *vs.* amine concentration are shown. Linear plots are obtained in all cases except for TBA quenching of PSF. Here the effect of organization is more noticeable than in the quenching of the singlet state. Rate constants for the quenching by TEOA are a factor close to 40 higher in BHDC than in the homogeneous solvent. The quenching mechanism probably involves a combination of intramicellar processes and intermicellar quencher exchange, since the mean occupation number by TEOA is close to one. It can also be observed here that the effect of the RMs is higher in the case of PSF. The increment is by a factor of 43 to be compared with 34 in the case of SF. On the other hand, the quenching by TBA is now observable due to the much longer

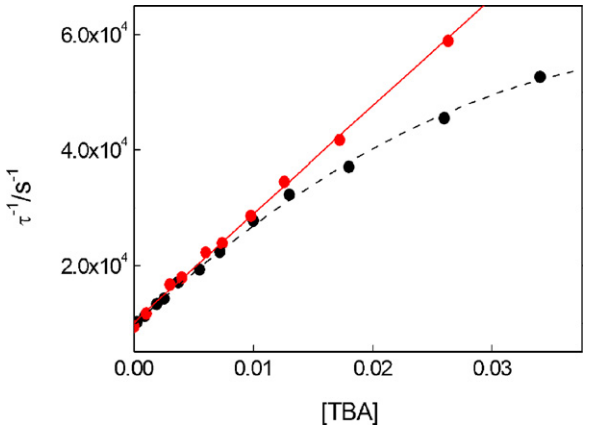


Fig. 6. Triplet quenching by TBA of SF (black) and PSF (red) in BHDC 0.05 M, $w = 15$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

lifetime of the excited state, and is one order of magnitude lower than in MeOH. A linear plot is obtained for the quenching of PSF while SF presents a downward curvature. In MeOH a similar curvature was observed for the quenching of PSF [16] by several aliphatic amines, and it was ascribed to a fast proton transfer equilibrium in the excited state. Why it is not observed for the same dye in RMs while it is noticeable for SF is not clear. In RMs the quenching scenario may be complicated by a saturation effect of the interface by the amine, and a consequent lower efficiency of quenching as the concentration increases. This effect may operate in a different way according to the location of the dye. For comparison, the rate constants obtained from initial slopes of plots of $1/\tau$ *vs.* [amine] are given in Table 4. It can be seen that the quenching by TBA is much less effective in the RMs than in a homogeneous solvent.

In summary, in BHDC RMs both dyes are located in the interface between the surfactant layer and the water pool. This produces important changes in the photophysical properties, which depend on the water content sensing a more polar environment when w increases. Nevertheless, even at the higher values of w investigated the photophysical parameters are far from those in pure water. Although both dyes are in the interface, PSF is more exposed to the water molecules than SF.

The hydrophilic quencher TEOA is very much more efficient in terms of the analytical concentration in the reverse micellar system. The same quenching efficiency is obtained with a concentration 100 times lower in the case of the triplet state. This is an important point in relation to applications of the dyes as a source of active radicals in bimolecular processes.

Acknowledgments

Financial support from the Agencia Nacional de Promoción Científica (PICT 2213/07) CONICET (PIP 2010-0284) and Universidad Nacional de Río Cuarto is gratefully acknowledged. G.V.P. and E.M.A. thank CONICET for a post-doctoral research fellowship.

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