Journal of Photochemistry and Photobiology A: Chemistry 252 (2013) 31–36

Contents lists available at SciVerse ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

Effect of the interface on the photophysics of eosin-Y in reverse miceles

Ernesto M. Arbeloa, Gabriela V. Porcal, Sonia G. Bertolotti, Carlos M. Previtali *

Departamento de Química, Universidad Nacional de Río Cuarto, 5800 Río Cuarto, Argentina

ARTICLE INFO

Article history:
Received 7 August 2012
Received in revised form 5 November 2012
Accepted 11 November 2012
Available online 21 November 2012

Keywords:
Eosin-Y
Photophysics
Triplet state
Reverse micelles
AOT
BHDC

ABSTRACT

The photophysics of the xanthene dye eosin-Y (Eos) was studied in reverse micelles (RMs) of sodium 1,4-bis (2-ethylhexyl) sulfosuccinate (AOT) and benzylhexadecyldimethylammonium chloride (BHDC). Special interest was assigned to the effect of organization on the triplet state properties. In the reverse micellar media both the absorption and emission spectra of the dye present a red shift with respect to water. It is concluded that Eos in both reverse micellar systems is localized in the interface. Although this is predictable in BHDC due to the positive charge at the interface and the negative charge of the dye, it is notable in the case of the negative interface of AOT. In this case it may be concluded that Eos resides in the interface co-micellizing with the surfactant, although more exposed to water than in the case of BHDC. Triplet state decay kinetics and absorption spectra were determined by laser flash photolysis. The triplet lives longer in RMs than in homogeneous solvents. The compartmentalization of the dye precludes the auto-quenching which shorts the lifetime in homogeneous solvents. The quenching by aliphatic amines was also investigated. The hydrophilic triethanolamine (TEOA) is localized in the water pool, and the triplet quenching is more efficient than in homogeneous solvents. On the other hand the quenching by tributylamine (TBA) which is located in the bulk organic solvent is much less efficient. The quenching by TEOA in RMs can be understood in terms of an exchange mechanism between micelles. Quantum yields of radicals produced in the triplet quenching process were determined.

1. Introduction

The study of the behavior of synthetic dyes in organized media is of interest because of the resemblance of these systems with many biological and chemical structures in nature. In an organized media e.g., micelles, reverse micelles, the reactants are confined within a small region, a few nanometer in size. The local properties like polarity, viscosity and pH are vastly different from those in homogeneous medium [1]. Consequently, the physical and chemical properties of dyes may undergo dramatic changes in these systems. These changes are useful to characterize the so-called microenvironmental properties, including local polarity (micropolarity) and local viscosity (microviscosity) of micellar systems. The photophysics of dyes provides a useful tool for investigate these properties [2] and the information gained in this way is very important from both an applied and a fundamental point of view [3]. For example, these studies are of interest with regard to micellar systems as a reaction medium because they affect both the kinetics and the mechanism of a specific reaction [4,5]. They are also important in many applications of electronic energy transfer, which may include photosensitized reactions and the micelle enhanced emission detection in analytical techniques [6]. In these systems donor, acceptor and micelle concentrations may be high enough to allow considerable energy transport between neighboring micelles.

On the other hand, the understanding of the interactions between ionic dyes and charged surfaces is of interest in numerous applications ranging from the design of electronic devices to the characterization of drug-delivery systems.

The photophysics and photochemistry of xanthene dyes, in particular eosin-Y, have been of widespread interest. These dyes are frequently used as laser dyes, fluorescent probes, biological stains, sensitizers, etc. Eosin-Y (Eos) sensitized nanoparticles were also employed to produce hydrogen by photocatalytic decomposition of water [7].

The photophysics of xanthene dyes were investigated in normal [8–11] and reverse micelles [12] generally by means of fluorescence spectroscopy. Reorientation of xanthene dyes in the interior of AOT was studied [13] and it was found that the water content of the reverse micelles has an important effect on the rotational dynamics of the probe. In particular, the photophysics and photochemistry of Eos in reverse micelles has received much less attention. The interaction of Eos with TiO_2 nanoparticles in AOT was previously investigated by means of fluorescence spectroscopy [14]. Photoinduced electron transfer from Eos and ethyl eosin to $Fe(CN)_6^{3-}$ in AOT reverse micelles was studied by Willmer and Joselevich [15].

* Corresponding author.
E-mail address: cprevitali@exa.unrc.edu.ar (C.M. Previtali).

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http://dx.doi.org/10.1016/j.jphotochem.2012.11.003

However, to the best of our knowledge, not detailed investigation of how the confinement in reverse micelles affect the excited states of the dyes can be found in the literature.

In this paper we present a study of the photophysics of Eos in reverse micelles (RMs) of AOT and BHDC. It was of special interest to investigate the effect of the charge of the interface, negative in the case of AOT and positive for BHDC, on the photophysics of the dye. Special interest was assigned to the effect of RMs on the triplet state properties, since it is responsible for many of the application of the dye as photosensitizer. In particular, Eos was used as a sensitizer of photopolymerization in aqueous medium. In the presence of electron donors such as tertiary amines, Eos has been described as efficient photoinitiator for the free radical polymerization of acrylate monomers [16–20] and styrene [21]. In a comparative study of the efficiency of several xanthene dyes Eos was among the most effective to initiate vinyl polymerization of acrylamide [22]. More recently, Eos in the presence of amine has been used as an efficient photoinitiator for surface modification by surface-mediated polymerization [23]. The photoinitiation mechanism in all cases involves an electron transfer from the co-initiator to the triplet state of the dye.

2. Experimental

Eosin-Y (Eos) was obtained from Aldrich and used without further purification. Sodium 1,4-bis (2-ethylhexyl) sulfosuccinate (AOT) from Sigma was dried under vacuum over P_2O_5. n-Heptane and ethanol were from Sintorgan (HPLC grade) and used as received. Water was HPLC grade from Sintorgan. The surfactant benzylhexadecyldimethylammonium chloride (BHDC) from Fluka was twice recrystallized from ethyl acetate and dried under vacuum. Benzene and methanol were from Sintorgan (HPLC grade) and used as received.

Reverse micelles solutions were prepared by dissolving the surfactant in the organic solvent, n-heptane for AOT and benzene in the case of BHDC. A small amount of Eos dissolved in water was added to these micellar solutions, so that the final total analytical concentration of the dye was less than 10^{-5} M. The micellar water content, $w = [H_2O]/[\text{Surfactant}]$, was adjusted by adding pure water up to desired ratio. The surfactant concentration was kept constant at 0.2 M for AOT and 0.05 M for BHDC. It is not possible to work at $w > 20$ in BHDC because at room temperature the solutions become cloudy. The aggregation number of BHDC in benzene is in the range from 100 ($w = 10$) to 400 ($w = 20$) [24], while for AOT in n-heptane it goes from 60 at $w = 6$ to 500 at $w = 30$ [25]. Accordingly, the mean occupation number of the dye is $\leq$0.03 in AOT, while in BHDC it is $\leq$0.1. Triethanolamine (TEOA) and tributylamine (TBA) both form Aldrich, were purified by vacuum distillation before use. In the quenching experiments small aliquots of a concentrated aqueous solution of TEOA was added to the RMs. In the case of TBA the amine was added as the pure compound.

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 498 nm. Transient absorption measurements were carried-out by excitation at 532 nm using a laser flash photolysis equipment as previously described [26]. The samples were deoxygenated by bubbling during 15 min with organic solvent-saturated high purity argon.

Fluorescence quantum yields were determined relative to Eos methanolic solution, $\Phi_F = 0.60$ [27].

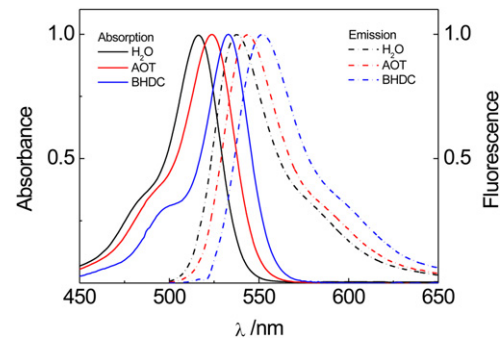

Fig. 1. Absorption spectra and fluorescence emission spectra of Eos in water, AOT/heptane (0.2 M, $w = 20$) and BHDC/benzene (0.05 M, $w = 15$).

3. Results and discussion

3.1. Singlet state

The absorption and fluorescence spectra of Eos in water and in RMs are shown in Fig. 1. At neutral and alkaline pH Eos is in its dianionic form with $\lambda_{max} = 516$ nm in water [28]. In the reverse micellar media both the absorption and emission present a red shift with respect to water. The shift in the absorption is 8 nm in AOT and 17 nm in BHDC. Similarly the red shift in the emission is more important in the case of BHDC.

The solvent and normal micelles effect on the spectral behavior of Eos was recently reported by Chakraborty and Panda [11]. They found that decreasing the solvent polarity produces a red shift both in the absorption and emission of the dye. They also reported a red shift in the presence of cationic surfactants. This red shift in the case of the absorption is of the same order of the one we find in RMs. Therefore, it might be concluded that Eos in both reverse micellar systems is sensing a less polar environment. This is probably the correct conclusion in BHDC, where the negative dye molecules are in the palisade region of the reverse micelles. However, in the case of AOT the red shift is noticeable up to $w = 30$ when it is generally accepted the center of the water pool presents characteristics of bulk water [29]. In Fig. 2 the effect of the water content on wavelength at the maximum in absorption and emission is presented. In BHDC at $w > 10$ the spectral shift is stabilized, while in AOT a trend toward the value of pure water is apparent although it is not reached even at $w = 30$.

Fluorescence quantum yields (Φ_F) and lifetimes (τ) are collected in Table 1. It can be seen that quantum yields are higher and lifetime

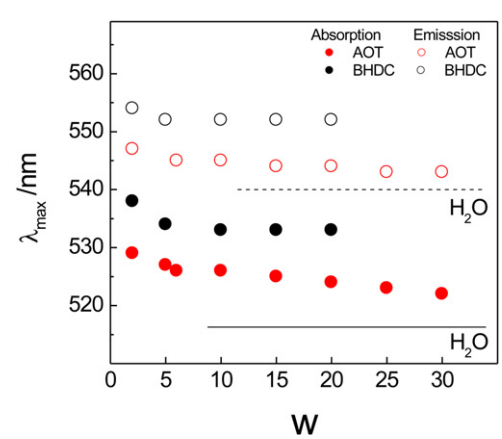

Fig. 2. Maximun wavelength in absorption and emission of Eos in AOT and BHDC as a function of the water content. The horizontal lines represent the value in pure water.

Table 1
Fluorescence quantum yield (Φ_F) and lifetime (τ) of Eos in reverse micelles.

	AOT		BHDC	
w	Φ_F	τ/ns	Φ_F	τ/ns
2	0.54	2.65	0.67	3.25
5	0.48	2.30	0.61	3.09
10	0.46	2.09	0.59	3.01
15	0.41	1.94	0.57	2.97
20	0.39	1.84	0.56	2.95
25	0.36	1.73	–	–
30	0.33	1.64	–	–
H_2O[a]	0.20	1.43	–	–
MeOH[a]	0.60	3.28	–	–

[a] From ref. [27].

are longer than in pure water at all w, and of the same order than in methanol [27] at low water content. Both quantities decreases with an augment of w, nevertheless in BHDC they go to a plateau at $w = 15$. The trend follows closely that shown in Fig. 2 for the spectral data. It can be concluded that both in AOT and BHDC RMs Eos resides in the interface co-micellizing with the surfactant, although more exposed to water in the case of AOT.

3.2. Triplet state

The transient absorption spectra of Eos in water and RMs, taken at short and long times, are shown in Fig. 3.

The spectrum at short times after the laser pulse can be ascribed to triplet–triplet transitions. In water the triplet spectrum is unchanged from pH 4 to pH 12 [30]. Here again a red shift in the spectrum with respect to water is observed in micellar medium. This effect is more evident in the case of BHDC. Apparent maxima are at 560, 570 and 580 nm in water, AOT and BHDC respectively. A lower intensity band around 400 nm is present in the three media that can be also ascribed to the triplet state. The long time spectrum in water presents two bands at 400 and 460 nm which correspond to the semireduced and semioxidized forms of the dye, respectively [31]. In water these species are formed in a self-quenching of the triplet by the ground state of the dye. The self-quenching rate constant was reported as $3.7 \times 10^8\ M^{-1}\ s^{-1}$ [9]. In the RMs this mechanism is precluded by the compartmentalization and low occupation number. This results in a longer lived triplet in the RMs. It can be seen that the long time spectrum in AOT and BHDC in the region of 380–450 nm is similar to that at short times and the semireduced and semioxidized forms of the dye cannot be observed. However, a small amount of these species may be contributing to the absorption since the relative absorbances in this region are higher in the long time spectra in the RMs. The properties of the triplet state in water and the RMs are collected in Table 2.

It is known that the triplet quantum yield of Eos decreases when solvent polarity decreases [27]. In AOT the value is close to that in water while it is much less in BHDC confirming that in the last case the dye is sensing a medium of low polarity.

Table 2
Triplet state properties of Eos in water and RMs.

Medium	λ_{max}/nm	Φ_T	τ/μs
H_2O	560	0.6	60
AOT $w = 5$	580	0.6	120
AOT $w = 30$	570	0.8	170
BHDC $w = 2$	580	0.2	170
BHDC $w = 20$	580	0.2	170

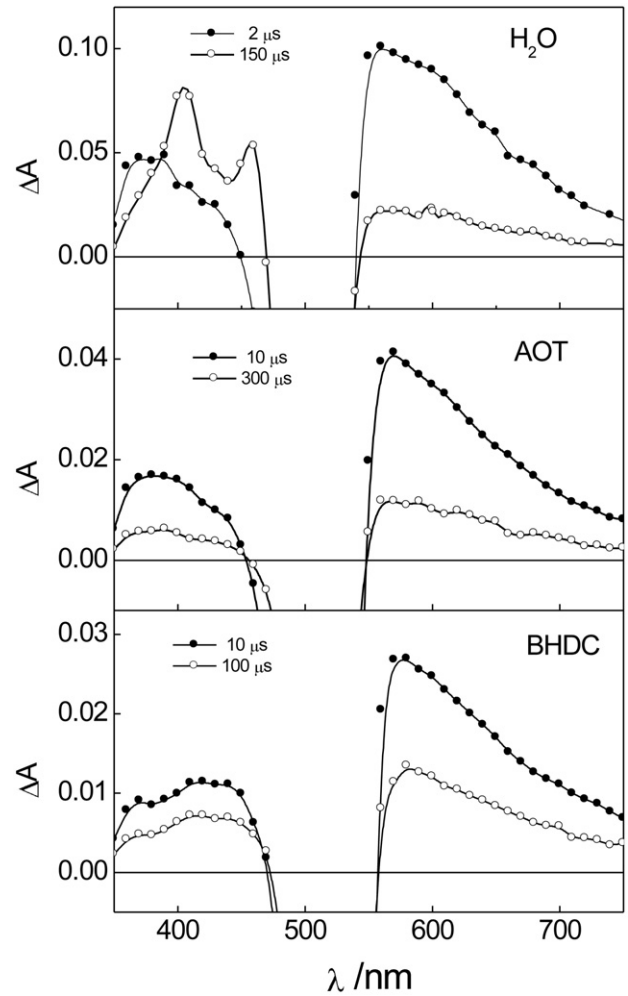

Fig. 3. Transient absorption spectrum of Eos in water, AOT and BHDC at different times after the laser pulse.

3.3. Triplet quenching by amines

Triethanolamine (TEOA) and tributylamine (TBA) have been used as electron donors in the polymerization of vinyl monomers photoinitiated by visible light using a dye as photosensitizer [22,32]. Since in these cases the generation of active radicals involves the quenching of the triplet state of the dye by the amine, we decided to investigate this process for Eos in reverse micelles.

The triplet decays monoexponentially in the presence of the amines. The apparent triplet quenching rate constant (k_q) was obtained from the triplet lifetime (measured by the T–T absorption at 580 nm) as a function of the amine concentration according to

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

where τ is the triplet lifetime, k_o is the first order rate constant for the triplet decay in the absence of the amine and [Am] is the analytical concentration of the amine.

In Fig. 4 a plot of $1/\tau$ vs. the analytical concentration of TEOA and TBA is presented in AOT and in BHDC. It should be noted that at the amine concentrations used in the triplet quenching experiments, singlet quenching was not observed in RMs.

The bimolecular rate constants for triplet quenching in homogeneous medium and in RMs are collected in Table 3. In homogeneous solvent they are of the order of magnitude expected for an excited state electron transfer process. For these reactions a correlation of

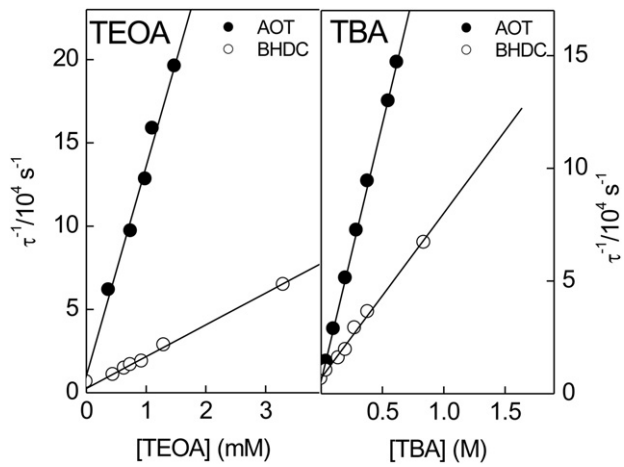

Fig. 4. Reciprocal of the triplet lifetime vs. the analytical concentration of TEOA and TBA in AOT and in BHDC.

the rate constants with the Gibbs energy change for the overall electron transfer process, ΔG°, is expected. The latter may be calculated from the redox potentials of the donor $E_{(D/D^+)}$ and acceptor $E_{(A/A^-)}$, and the energy E^* of the excited state involved, with the Rehm-Weller equation [33]

$$\Delta G^{\circ} = E_{(D/D^+)} - E_{(A/A^-)} - E* + C \quad (2)$$

where C is the coulombic energy term. From the literature data for Eos triplet energy and reduction potential [34] and amines oxidation potential [35] ΔG° can be estimated in a polar solvent with $C \sim 0.05$ eV [36]. The resulting values are −0.09 eV and +0.03 eV for the quenching by TBA and TEOA respectively. Rate constants of the order of $10^6\,M^{-1}\,s^{-1}$ can be expected for these values of the overall free energy change in the quenching of dyes by aliphatic amines [37]. Moreover, the higher value for TBA in MeOH is in line with the differences in ΔG°. On the other hand, the order of the rate constants is inverted in RMs. In the confined system they are three orders of magnitude higher for TEOA than for TBA. This can be explained by differences in location of the amines and the dye in the reverse micellar systems.

The quenching by TEOA in RMs can be understood in terms of an exchange mechanism between micelles. TEOA is a hydrophilic molecule (the octanol–water partition coefficient is 0.1) [38] and it is expected to be totally incorporated into the RMs partitioning between the water pool and the polar interface. Since the TEOA concentration in the quenching experiments varies from 1×10^{-4} to 1×10^{-3} M, the mean occupation number by TEOA is ≤1. It is expected that for a micelle containing a triplet Eos and one or more TEOA molecules a very fast, sub-microsecond, quenching takes places. Therefore, the observed decay of the triplet in the microseconds time scale should be due to an intermicellar exchange mechanism of the quencher. A kinetics scheme for the quenching in reverse micellar system, considering both intra and intermicellar processes, for a quencher Q totally incorporated into the micelles, leads to a non-exponential decay for the excited state. The decay kinetics of the excited state can be shown to be depicted by Eqs. (3)–(6) [39,40].

$$[T] = [T]_0 \exp[-C_1 t - C_2(1 - \exp(-C_3 t)] \quad (3)$$

$$C_1 = k_0 + \frac{n k_{qm} k_{ex}[M]}{k_{qm} + k_{ex}[M]} \quad (4)$$

$$C_2 = \frac{n k_{qm}^2}{(k_{qm} + k_{ex}[M])^2} \quad (5)$$

$$C_3 = k_{qm} + k_{ex}[M] \quad (6)$$

where k_{qm} is the unimolecular intramicellar quenching rate constant, k_{ex} is the rate constant for the exchange of solute between micelles and it will depend on the diffusion of two micelles in the organic pseudophase, n is the mean occupation number and $[M]$ is the micellar concentration. In the limit of

$$k_{qm} >> k_{ex}[M] \quad (7)$$

Eq. (3) reduces to

$$[T] = [T]_0 \exp[-(k_0 + k_{ex}[Q])t - n(1 - \exp(-k_{qm} t)] \quad (8)$$

Condition (7) is fulfilled in the present case if $k_{qm} \geq 10^6\,s^{-1}$ which is not an unreasonable value for the intramicellar quenching by a neutral quencher. Under our experimental conditions the Eos triplet lives ca. 200 μs in the RMs and in the presence of TEOA decays in several tens of microseconds. After a few microseconds the second terms in the square bracket is of the order of n and has no effect on the lifetime. In this case the decay becomes first order with a lifetime

$$\tau^{-1} = k_0 + k_{ex}[Q] \quad (9)$$

This interpretation of the quenching mechanism, with k_q in Eq. (1) equal to k_{ex} in Eq. (9), is further confirmed by the values we find for k_q, which are of the same order of those reported in the literature for the exchange rate constant between AOT reverse micelles in heptane [25,39] and isooctane [40] and for BHDC in benzene [24].

On the other hand, the quenching by TBA in RMs is lower than in homogeneous solvent. This can be explained taking into account the molecular structure of the amines. In a study of the partition of amines in AOT/hexane RMs, Zingaretti et al. [41] concluded that tertiary amines remain mostly in the organic phase. In fact, the partition coefficients were too small and could not be determined. Therefore, the low quenching efficiency observed for TBA in RMs could be a consequence of the poor access of the amine to the interface where the dye resides.

Table 3
Triplet quenching rate constants (k_q) in MeOH and RMs.

	Amine	k_q/M^{-1} s^{-1}
MeOH	TBA	3.2×10^6
	TEOA	1.1×10^6 [a]
BHDC 0.05 M (w = 20)	TBA	7.3×10^4
	TEOA	1.9×10^7
AOT 0.2 M (w = 30)	TBA	2.3×10^5
	TEOA	1.0×10^8

Estimated error ± 10%.
[a] Literature value: 1×10^6 in ethanol ([43]).

3.4. Radical yields

In the presence of the amines the long time transient absorption spectrum differs from that in the absence of the quenchers shown in Fig. 3. The remaining spectrum after the triplet quenching is depicted in Fig. 5 for the case of TEOA. The maximum of the absorption band is at 400 nm in AOT and at 410 nm in BHDC. It can be ascribed to the semireduced form of the dye [31].

The fraction of triplets intercepted by the quencher may be written as

$$f = \frac{k_q[Q]}{k_0 + k_q[Q]} \quad (10)$$

In the spectra shown in Fig. 5 f was higher than 0.9 in both cases. It can be seen that the yield of the semireduced dye is much higher in BHDC. Radical quantum yields were obtained according to

$$\Phi_R = \frac{\Delta A_R \varepsilon_T}{\Delta A_T \varepsilon_R} \Phi_T \quad (11)$$

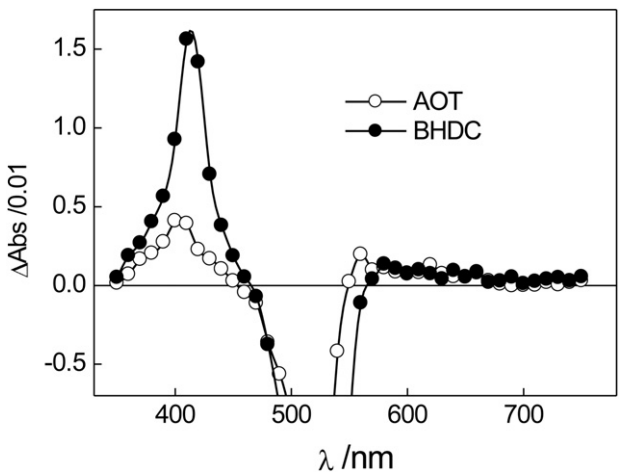

Fig. 5. Long time transient absorption spectrum of Eos in the presence of TEOA 5.6×10^{-4} M in AOT at $w = 30$ and 3.3×10^{-3} M in BHDC at $w = 20$.

Table 4
Quantum yields of semireduced Eos in RMs.

	Φ_R
BHDC/TEOA 3.3 mM[a]	0.024
BHDC/TBA 0.84 M[a]	0.053
AOT/TEOA 0.6 mM[a]	0.006
AOT/TBA 0.62 M[a]	0.26

[a] Analytical concentration.

Here ΔA_R is the long time absorption remaining after the triplet decay in the presence of TEOA measured at 410 nm, ΔA_T is the prompt T–T transient absorption measured at 580 nm immediately after the laser pulse, ε_R and ε_T are the respective molar absorption coefficients and Φ_T is the triplet quantum yield in the absence of the amine.

In order to determine Φ_R by means of Eq. (11) the absorption coefficients of the radical in all media are necessary. They were determined by the ground state depletion (GSD) method [42]. The transient negative absorbance difference at the maximum wavelength of the ground absorption, ΔA_G, was compared with the absorption at the maximum of the spectrum of the semireduced dye, ΔA_R, with the aid of Eq. (12).

$$\varepsilon_R = \left(\frac{\Delta A_R}{\Delta A_G}\right)\varepsilon_G \tag{12}$$

In Eq. (12) ε_R and ε_G are the molar absorption coefficients of the radical and ground state respectively, at the wavelengths of their absorbance maxima. The quantum yields obtained in this way are collected in Table 4.

The photoreduction by TEOA most likely occurs in the hydrated surface of the palisade, where the electron transfer quenching occurs according to

$$^3\mathrm{Eos}^{=} + \mathrm{TEOA} \rightarrow \mathrm{Eos}^{3-\bullet} + \mathrm{TEOA}^{+\bullet}$$

In AOT both radical ions remain in the interface and the lower Φ_R may be due to the fast recombination reaction of these species once they are formed. On the other hand, in BHDC the positive charge of the interface favors the charge separation by expelling the positive TEOA radical ion, which explains the higher Φ_R. In turn, the yields are very much higher for TBA, although at the expense of a very much higher amine concentration, and this reflects the separation of the initially formed radical ions pair in this case.

These results are important for application of the couple dye-amine as radical generation system in RMs. In particular, the system may be useful for the initiation of vinyl polymerization in RMs and in this way monodisperse polymer nanoparticles may result. Xanthene dyes/TEOA was found to be a useful photoinitiating system for vinyl polymerization in water [22]. In RMs high efficiency in triplet quenching is reached at an amine concentration one order of magnitude lower than in water. However the radical quantum yields are also one order of magnitude lower [22], with the exception of TBA, but in this case a much higher amine concentration is necessary. It is important to point out that the yields actually measured are for the semireduced form of the dye and it is assumed that active alkyl radicals originated from the amine are formed with the same yield.

In summary, the photophysics of the dye depends upon the nature of the surfactant used to form the RMs. In spite of the dye being in its dianionic form, the dye localizes in the interface of the reverse micelles both in AOT and BHDC. The main difference is that in AOT the photophysics parameters are sensitive to the size of the water pool. Nevertheless they do not reach the values in pure water even at the highest water content. On the other hand, in BHDC the photophysics senses a less polar environment, and it is practically independent of the water content. The triplet state lives longer in the RMs than in homogeneous solvent as a result of the suppression of the self-quenching process due to the compartmentalization.

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. E.M.A. and G.V.P. thank CONICET for a post-doctoral research fellowship.

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