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Photophysics and photochemistry of mercurochrome in reverse micelles



Marcela S. Altamirano, Micaela E. Grassano, Sonia G. Bertolotti, Carlos M. Previtali*

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

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ABSTRACT

The photophysics of the xanthene dye 2',7'-Dibromo-5'-(hydroxymercurio)fluorescein disodium salt (merbromine, mercurochrome) (Mcr) was studied in reverse micelles (RMs) of sodium 1,4-bis (2-ethylhexyl) sulfosuccinate (AOT) and benzylhexadecyldimethylammonium chloride (BHDC). 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 MCr in both reverse micellar systems is localized in the interface. In BHDC due to the positive charge at the interface and the negative charge of the dye, it remains anchored to the interface irrespective of the water content of the RMs. On the other hand in the case of the negative interface of AOT the photophysical properties tend to those in homogeneous water solution as the water content increases. For small size AOT RMs the dye resides in the interface co-micellizing with the surfactant, although more exposed to water than in the case of BHDC. Special interest was assigned to the effect of confinement on the triplet state properties. The 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. Furthermore, the quenching by electron donors and acceptors was investigated. Two aliphatic amines were used as electron donors. The hydrophilic triethanolamine (TEOA) is localized in the water pool, and the triplet quenching is more efficient than in homogeneous solvents. The apparent quenching rate constant for TEOA in AOT is one order of magnitude higher than BHDC. On the other hand the quenching by dipropylamine (DPA) 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. As electron acceptor 1,4-benzoquinone (BQ) was employed, and the value in BHDC is two orders of magnitude higher than in AOT. These divergences most likely arise from different partitions of the quenchers in the reverse micellar systems.

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1. Introduction

Reverse micelles (RMs) are frequently considered as self-organized nano-reactors. In these systems, the reactants are confined within a small region, a few nanometers in size, and the reactivity and products properties of different processes may differ dramatically from those in homogeneous solutions. In the interior of RMs the local properties like polarity, viscosity and pH are vastly different from those in homogeneous medium [1]. Consequently, the physical and chemical properties of confined molecules may undergo dramatic changes in these systems. These changes are also 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 as well 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

* Corresponding author.

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

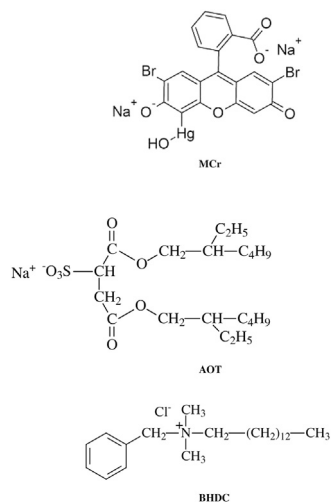
characterization of drug-delivery systems. RMs are also particularly appropriate to the synthesis of nano-scale materials. In the last years there has been a continuing interest in reverse micellar systems where polar solvents other than water are used [7,8]. This is in part due to potential application in nanomaterial synthesis when the synthesized material should have solubility in nonaqueous medium for further applications [9]. Recently we employed RMs formed by the cationic surfactant benzyl-hexadecyl-dimethylammonium chloride (BHDC) to synthesize latex nano particles of polyacrylamide using a dye as visible photosensitizer of polymerization [10].

In this paper we present a study of the photophysics and photochemistry of the xanthene dye 2',7'-dibromo-5'-(hydroxymethyl) fluorescein disodium salt, commonly known as merbromin or mercurochrome (MCr) in reverse micelles formed by sodium 1,4-bis (2-ethylhexyl) sulfosuccinate (AOT)/heptane or BHDC/benzene. In Scheme 1 the structures of the dye and surfactants are shown. The photophysics of xanthene dyes were investigated in normal [11–14] and reverse micelles [15,16] generally by means of fluorescence spectroscopy. Reorientation of xanthene dyes in the interior of AOT was studied [17] and it was found that the water content of the reverse micelles has an important effect on the rotational dynamics of the probe. However, the photophysics and photochemistry of MCr in homogeneous and micro-heterogeneous systems was much less studied than other xanthene dyes.

MCr is often used as an antiseptic and antibacterial substance. At pH values ranging from 5.5 to 10.0 proved to be highly fluorescent with a quantum yield of 0.2 [18]. However, the presence of heavy atoms in the molecule gives rise to an efficient intersystem crossing and a high room temperature phosphorescence emission signal can be observed when mercurochrome is immobilized on a solid support [19]. It was shown that MCr is a relatively efficient sensitizer for photodynamic action via singlet oxygen generation with a quantum yield of 0.14 in methanolic solution [20] and 0.23 in water (buffer pH 7) [15]. Unlike eosin, MCr is extremely resistant to light; it does not fade even when exposed to strong visible irradiation [21]. This makes this dye a very suitable choice for applications as sensitizer requiring long irradiation periods.

2. Experimental

Mercurochrome was obtained from Aldrich and was used without further purification. Sodium 1,4-bis (2-ethylhexyl)



Scheme 1. Chemical structures of the dye and surfactants.

sulfosuccinate (AOT) from Sigma was dried under vacuum over P_2O_5 . *n*-Heptane, benzene, methanol and water were from Sintorgan (HPLC grade) and used as received. The surfactant benzylhexadecyldimethylammonium chloride (BHDC) from Fluka was twice recrystallized from ethyl acetate and dried under vacuum. Triethanolamine (TEOA) and Dipropylamine (DPA) both from Aldrich, were purified by vacuum distillation before use. 1,4-Benzoquinone (BQ) from Aldrich was purified by sublimation.

Reverse micelles solutions were prepared by dissolving the surfactant in the organic solvent, *n*-heptane for AOT and benzene in the case of BHDC. The surfactant concentration was varied between 0.05 M and 0.2 M in both cases. A small amount of MCr dissolved in water (buffer pH 8) was added to these micellar solutions, so that the final total analytical concentration of the dye was less than 10^{-6} M. The micellar water content, $w = [H_2O]/[Surfactant]$, was adjusted by adding water (buffer pH 8) up to desired ratio. 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 ($w = 20$) [22], while for AOT in *n*-heptane it goes from 60 at $w = 6$ to 500 at $w = 30$ [23]. Accordingly, the mean occupation number of the dye is < 0.1 in all cases. In the quenching experiments small aliquots of a concentrated aqueous solution of the quencher were added to the RMs. In the case of DPA the amine was added as the pure compound.

Absorption spectra were obtained on a Hewlett Packard 6453E diode array spectrophotometer. Fluorescence spectra were measured with a Horiba Jobin Yvon Fluoromax-4 spectrofluorometer in air equilibrated solutions. Fluorescence quantum yields were determined relative to 4,5 dibromofluorescein 0.01 M in KOH/ethanol [24]. Fluorescence lifetimes were determined by time-correlated-single-photon-counting (SPC) with a FL 900 Edinburgh Instruments equipped with a PicoQuant sub-nanosecond pulsed LED emitting at 498 nm. The fluorescence decays were analyzed by a deconvolution method provided by Edinburgh Instruments. The quality of the fitting was judged by the reduced chi-square (χ^2) values and the distribution of the weighted residuals. In all cases a mono-exponential fit was satisfactory, the χ^2 value was close to unity and the weighted residuals were distributed randomly along the spanned time interval.

Transient absorption measurements were carried-out by excitation at 532 nm using a laser flash photolysis equipment as previously described [25]. The samples were deoxygenated by bubbling during 15 min with organic solvent-saturated high purity argon.

3. Results and discussion

3.1. Absorption and fluorescence

The absorption and fluorescence spectra in water, methanol and RMs are shown in Figs. 1 and 2 respectively.

In Table 1 the photophysical parameters of the dye in different media are collected. It is well-known that the maxima in the absorption and fluorescence spectra of xanthene dyes are red shifted as medium polarity decreases. Furthermore, fluorescence lifetime increases as solvent polarity decreases [26]. Therefore, the photophysical parameters in AOT presented in Table 1 point to the dye molecules located in a region of micropolarity lower than water although due to the negative charge it is expected to be located in the water pool of the RMs. The absorption and fluorescence parameters in BHDC are an indication that MCr is sensing a region of polarity lower than MeOH. This can be explained by the negative dye molecules anchored to the interface in the positive palisade (the layer immediately below the micellar surface) of the RMs. On the other hand in AOT at low w the dye is in close proximity with

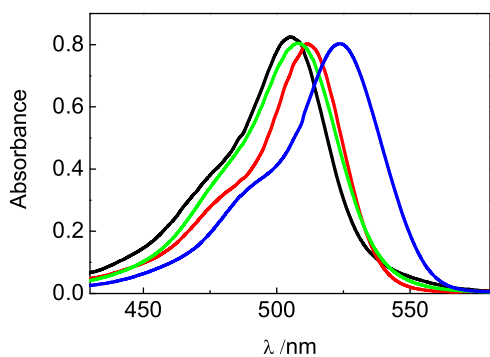


Fig. 1. Absorption spectra of MCr in water (pH 8) (black), MeOH (red), AOT/heptane $w=40$ (green) and BHDC/benzene $w=20$ (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

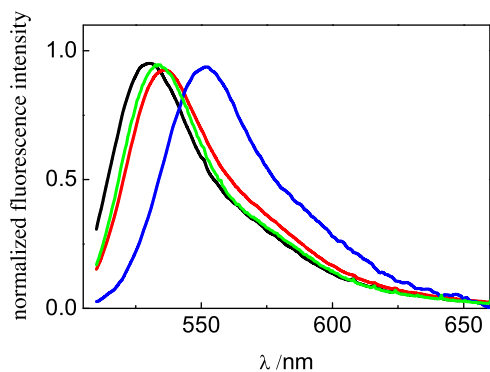


Fig. 2. Fluorescence spectra of MCr in water (pH 8) (black), MeOH (red), AOT/heptane $w=40$ (green) and BHDC/benzene $w=20$ (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Photophysical Parameters in different media.

	$\lambda_{(\max)}\text{abs/nm}$	$\lambda_{(\max)}\text{fluor/nm}$	τ_f/ns	Φ_F	$\lambda_{(\max)}\text{T-T/nm}$
Water pH 8	505	530	2.0	0.22	360; 420(s); 560
MeOH	512	536	3.1	0.51	350; 430(s); 565
AOT $w=5$	512	534	2.8	0.29	370; 570
AOT $w=40$	508	532	2.1	0.27	360; 560
BHDC $w=5$	525	552	3.4	0.68	360; 410; 580
BHDC $w=20$	524	552	3.3	0.62	360; 430; 570

the surfactant interface and the fluorescence behavior reflects a region of lower polarity than water, although not comparable to that in BHDC. The size of RMs is a primarily a function of the water content, as given by w [23]. Increasing the water content in AOT induces a movement of the dye molecules to the water pool and the photophysical behavior approaches that in water solution, although not reaching the values in bulk alkaline water. In Fig. 3 typical plots of the fluorescence decay dependence on w are shown.

In Fig. 4 the fluorescence lifetime is shown as a function of the water content of the RMs. In BHDC the fluorescence quantum yield are the largest and lifetimes the longest. They are practically independent of the water content. It can be concluded that in this system the dye remains in a region of low polarity, close to the organic phase, at all w values. In the case of AOT the fluorescence

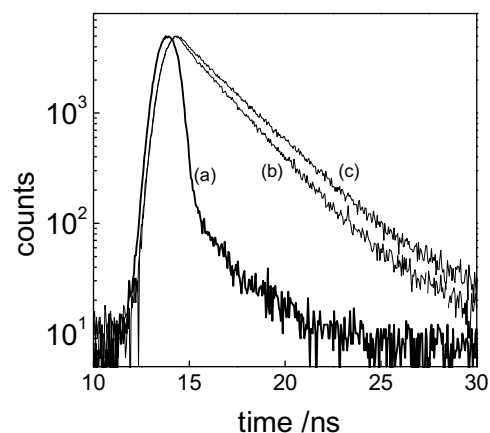


Fig. 3. SPC fluorescence decay traces of MCr in RMs of AOT/heptane. (a) Lamp profile; (b) $w=50$; (c) $w=10$.

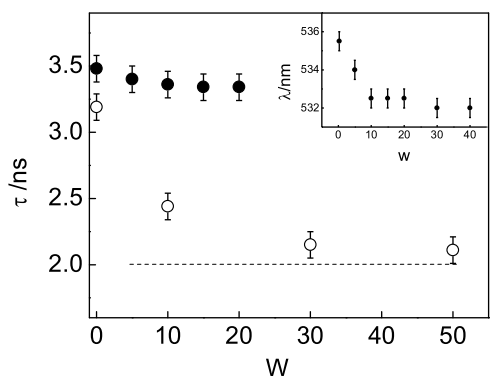


Fig. 4. Fluorescence lifetime of MCr in reverse micellar systems as a function of the water content (●) BHDC (○) AOT. The dash line is the value in water. Inset: Maximum emission wavelength as a function of the water content in AOT.

quantum yield is intermediate between water and methanol and shows a slight decrease on increasing w . Also a decrease in lifetime is noticeable as w increases, but the value in water is not reached even at $w=50$. The effect of the water content on the fluorescence spectrum in AOT is shown in the inset in Fig. 4. Also in this case at the higher value of w the maximum is red shifted by two nm with respect to pure water. It is interesting to note that the parameters stabilize for $w > 20$ and become nearly independent of the water content.

3.2. Triplet state

The excited triplet state of the dye was investigated by means of laser flash photolysis. The transient absorption spectra of MCr in various media upon laser pulse excitation at 532 nm are shown in Fig. 5. The apparent maxima present immediately after the laser pulse are collected in Table 1.

At short times the difference transient absorption spectrum in buffer presents two maxima at 370 and 555 that can be ascribed to the T-T transition. In MeOH the spectrum is similar but the maximum in the visible is now at 365 nm. In AOT RMs the spectrum is very alike to that in water, except at very low water content. In BHDC the maximum in the visible is at 570 nm but now it presents two maxima in the UV at 360 and 420 nm. In the latter medium the spectrum is the same at $w=10$ or 20. It is important to note that, since these are difference spectra, the maximum of the apparent bands of the T-T transitions is affected by the bleaching

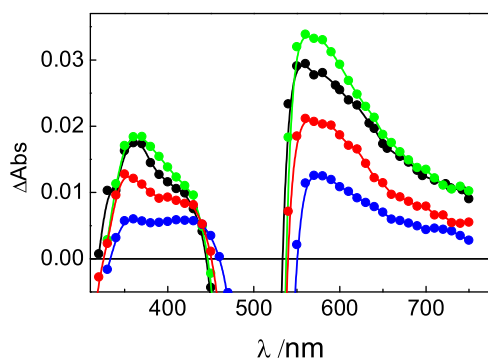
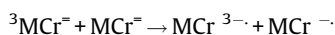


Fig. 5. Transient absorption spectra of MCr taken at 5 μs after the laser pulse in buffer pH 8 (black); at 2 μs in MeOH (red); at 1 μs in AOT 0.1 M $w=20$ (green) and at 2 μs in BHDC $w=20$ (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

due to ground state absorption which in turns changes with the medium, see Fig. 1. Accordingly, the apparent maximum at 420 nm in BHDC is most likely an effect of the red shifted position of the bleaching, and therefore the difference spectrum shows now a T–T absorption band that is hidden by the bleaching in the other media. In both reverse micellar media the spectrum is independent of the detergent concentration in the range 0.05–0.2 M.

After the triplet decay an absorption in the region 300–500 nm remains, in all cases, it is more important in the case of homogeneous solvents and in BHDC than in AOT. The spectral characteristics of the species formed after the triplet decay can be explained in terms of the self quenching of the triplet dye by ground state molecules. The semioxidized radical and the semi-reduced forms are formed this process. MCr exist mainly as a dication at $\text{pH} > 7$ [27] and the self quenching reaction may be written as



The semireduced form absorbs in the region of 360–400 nm with λ_{max} depending of the pH and polarity of the medium, while the semioxidized form is expected to absorb around 440 nm, by analogy with other xanthene dyes [28]. This is confirmed by the transient spectra in the presence of electron donors and acceptors resulting by the electron transfer quenching of the triplet state. The self quenching rate constant in buffer pH 8 was determined as $1.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. In RMs the self quenching process must take place by an intermicellar process, since the occupation number is < 0.1 . This is the cause of the longer triplet lifetime observed in these media under similar experimental conditions.

3.3. Triplet quenching by amines and 1,4-benzoquinone

Aliphatic amines have been used as an electron donor in the polymerization of vinyl monomers photoinitiated by visible light using synthetic dyes as photosensitizer [29,30]. It was demonstrated that the initiation mechanism involves the generation of active radicals through the quenching of the triplet state of the dye by the amine. Since MCr was employed as a sensitizer in these photopolymerization studies, and the feasibility of conducting the polymerization process in reverse micelles afford a means of obtaining nanoparticles of high molecular weight and a narrow size distribution [31] it was of interest to investigate the triplet quenching processes for MCr in RMs by potential co-initiators of vinyl polymerization.

Triethanolamine (TEOA) and dipropylamine (DPA) were employed as electron donors for triplet quenching. In Figs. 6 and 7 the transient absorption spectra of the dye in the presence of

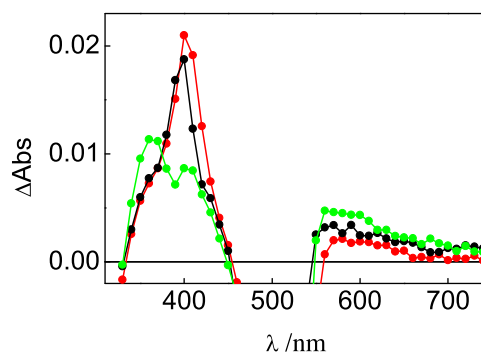


Fig. 6. Transient absorption spectra of MCr in the presence of DPA. MeOH (DPA 0.066 M) at 180 μs after the laser pulse (black); BHDC ($w=10$, DPA 0.095 M) at 350 μs after the laser pulse (red); AOT ($w=10$ DPA 0.018 M) at 450 μs after the laser pulse (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

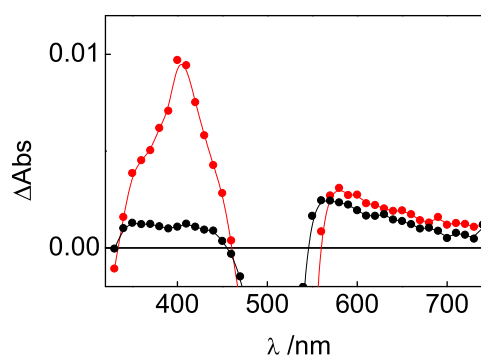


Fig. 7. Transient absorption spectra of MCr in the presence of TEOA. BHDC ($w=10$, TEOA 3 mM) at 300 μs after the laser pulse (red); AOT ($w=10$, TEOA $3.5 \times 10^{-4} \text{ M}$) at 450 μs after the laser pulse (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

DPA and TEOA are shown in homogeneous and RMs media. The maximum ca. 400 nm was attributed to the semireduced dye formed in Reaction (2)



A similar process was observed in water in the quenching by triethanolamine [27].

The spectra in Fig. 6 show that in AOT the radical yield is much less than in BHDC in spite of the triplet being quenched to the same extent. It must be noted that DPA is a molecule of low solubility in water and it is probably partitioned between the bulk organic phase and the inner interphase of the reverse micelle.

The water soluble TEOA is located mainly in the water pool and the electron transfer process takes place in the interphase where the dye molecules reside. The differences in the spectra between AOT and BHDC are probably due to the fast recombination of the radicals in AOT due to the confined environment where the electron transfer quenching takes place.

Vinyl polymerization can also be initiated by photooxidation of a dye by strong electron acceptors [32]. To explore the interaction of MCr excited triplet with an electron acceptor we have investigated the triplet quenching by BQ. It was found that both in homogenous system and in RMs the semioxidized form of the dye was generated by laser flash excitation in the presence of BQ. In Fig. 8 the transient absorption spectra in the presence of BQ is shown. In this case after the triplet decay it is evident that a long lived transient with a maximum at 440 is present in BHDC, while in

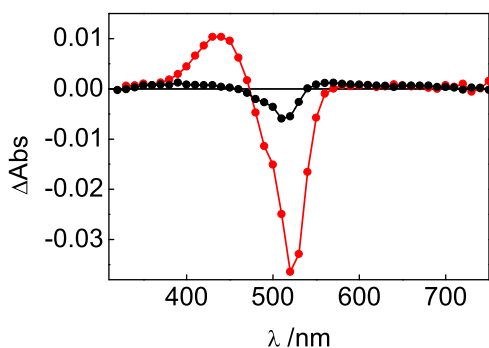


Fig. 8. Transient absorption spectra of MCr in the presence of BQ, BHDC ($w = 10$, BQ 1.1×10^{-5} M) at $100 \mu\text{s}$ after the laser pulse (red); AOT ($w = 10$, BQ 2×10^{-4} M) at $180 \mu\text{s}$ after the laser pulse (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

AOT the dye has mostly recovered, with a very low yield of radicals. This absorption can be ascribed to the semioxidized form of MCr by analogy with other xanthene dyes [25]. The broad band with maximum at 440 also contains a contribution for the radical anion of BQ, absorbing at 460 nm, but with a lower absorption coefficient than the semioxidized dye [33].

In the presence of the quenchers the triplet decays mono-exponentially. Apparent triplet quenching rate constants (k_q) were determined by triplet lifetime (measured by the T–T absorption at 580 nm) as a function of quencher concentrations according to:

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

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 $[Q]$ is the analytical concentration of the quencher.

In Figs. 9 and 10 plots of $1/\tau$ vs. the analytical concentrations of TEOA and BQ respectively are presented. It should be noted that at the quenchers concentrations used in these experiments, singlet quenching was not observed. The quenching rate constants were additionally determined in MeOH and all the results are collected in Table 2.

In order to understand the differences in the apparent quenching rate constants several factors must be considered. In a homogeneous solvent the quenching efficiency depends on the electron donor or acceptor capability of the quencher. Thus rate constant for DPA, with a potential of 1.02 V is two order of magnitude lower than that of TEOA (0.90 V) in MeOH [34]. BQ is a very efficient electron acceptor ($E_{1/2} = 0.50$ V [35]) and its rate constant is the higher in the homogeneous solvent. On the other hand, in RMs the order of the rate constants does not correlate with

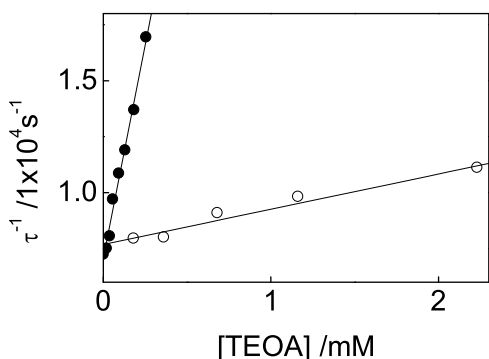


Fig. 9. Triplet quenching by TEOA in BHDC (○) $w = 10$ and AOT (●) $w = 10$.

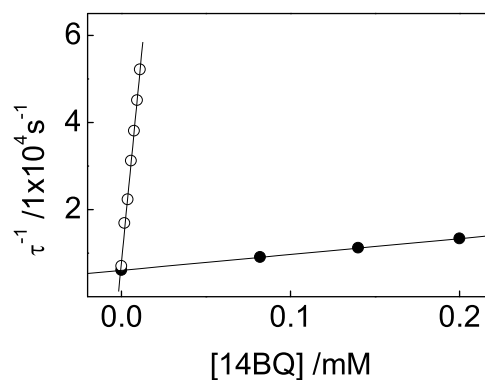


Fig. 10. Triplet quenching by BQ in BHDC (○) $w = 10$ and AOT $w = 10$ (●).

Table 2

Triplet quenching rate constants in units of $\text{M}^{-1} \text{s}^{-1}$.

	MeOH	AOT $w = 10$	BHDC $w = 10$
DPA	2×10^5	2×10^5	1×10^5
TEOA	1.3×10^8	3.8×10^7	1.6×10^6
BQ	6.6×10^8	3.6×10^7	4.0×10^9

the electron transfer reaction free energy change. While for DPA the rate constants are the lowest and of the same order in all of system studied, for TEOA it is higher than for DPA. In AOT it is similar to the homogeneous solvent, but it is one order of magnitude lower in BHDC. On the other hand, for BQ the highest value is in BHDC, two orders of magnitude higher than in AOT, which in turn is lower than in MeOH. These divergences most likely arise from different partitions of the quenchers in the reverse micellar systems.

TEOA, being a hydrophilic molecule, is most likely in the water pool of the RMs. However, at the concentration employed in the quenching experiments in AOT the mean occupation number is in the range 0.1–0.5, therefore, the quenching mechanism probably involves a combination of intramicellar processes and intermicellar quencher exchange. Similarly to the quenching of eosin in reverse micelles [13] the rate constant in AOT is one order of magnitude higher than in BHDC although for the quenching of MCr triplet they are much lower than for the quenching of eosin. This reflects a different location of MCr, deeper in the interfacial region closer to the organic phase than that of eosin.

BQ is mostly in the bulk organic phase, the high value for the rate constant in BHDC is an indication of the preference of BQ for the aromatic components of the hydrophobic tails of the surfactant molecules. From the absorption and fluorescence spectra of MCr its location can be estimated as in close proximity to the organic phase, therefore a higher local concentration of BQ in the proximities of the dye is to be expected.

In summary, the excited state properties of the dye depend upon the nature of the RMs. In anionic AOT, in spite of MCr being in its dianionic form, the dye localizes in the interface, sensing a medium of micropolarity similar of that of MeOH. The photophysics is sensitive to the size of the water pool. However, absorption and fluorescence parameters do not reach the values in pure water even at the highest water content. On the other hand, in BHDC the photophysics and the photochemical behavior can be explained by an exposition of MCr molecules to potential quencher of the excited states localize in the organic phase. Accordingly the yield of radicals in the electron transfer quenching of the dye, depends upon the type of quencher and surfactant employed.

Acknowledgments

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References

- [1] A. Ueda, T. Kimura, Investigation of the micropolarity of reverse micelles using quinolinium betaine compounds as probes, *J. Colloid Interface Sci.* 163 (1994) 515–516; C. López-Quintela, M.C. Tojo, J.R. García Río, Microemulsion dynamics and reactions in microemulsions, *Curr. Opin. Colloid Interface Sci.* 9 (2004) 264–278.
- [2] R. Rafiq, Microviscosity inside a nanocavity: a femtosecond fluorescence up-conversion study of malachite green, *J. Phys. Chem. B* 114 (2010) 13988–13994; Q. L. Zhang, J. Yin, Q. Su, Local Polarity and Microviscosity of the Interior of Dendritic Polyethylene Amphiphiles, *Macromolecules* 44 (2011) 6885–6890; S. Ghosh, C. Mandal, N. Govind Rao, Photophysics of 3,3'-Diethyloxadicarbocyanine Iodide (DODCI) in ionic liquid micelle and binary mixtures of ionic liquids: effect of confinement and viscosity on photoisomerization rate, *J. Phys. Chem. B* 116 (2012) 9482–9491.
- [3] I.A. Kondo, Reactive dynamics in micelles: auramine O in solution and adsorbed on regular micelles, *J. Phys. Chem. B* 114 (2010) 12859–12865; J.J. Correa, R.E. Silber, N.E. Riter, Nonaqueous polar solvents in reverse micelle systems, *Chem. Rev.* 112 (2012) 4569–4602.
- [4] D. De, A. Datta, Modulation of ground- and excited-State dynamics of [2,20-Bipyridyl]-3,30-diol by micelles, *J. Phys. Chem. B* 115 (2011) 1032–1037; S. Manna, Effect of micellar environment on charge transfer dye photophysics, *J. Mol. Liq.* 168 (2012) 94–101.
- [5] G. Astray, A. Cid, L. Garcia-Río, P. Hervella, J.C. Mejuto, M. Pérez-Lorenzo, Organic reactivity in AOT-stabilized microemulsions, *Prog. React. Kinet Mech.* 33 (2008) 91–97; M. Marchena, F. Sanchez, Kinetics of Photochemical Reactions under Restricted Geometry Conditions, *Prog. React. Kinet Mech.* 35 (2010) 27–80.
- [6] Y. Hong, J.W.Y. Lam, B.Z. Tang, Aggregation-induce emission, *Chem. Soc. Rev.* 40 (2011) 5361–5388.
- [7] A. Setua, D. Chakraborty, M.U. Seth, P.V. Bhatta, N. Satyam, Synthesis, optical properties, and surface enhanced raman scattering of silver nanoparticles in nonaqueous methanol reverse micelles, *J. Phys. Chem. C* 111 (2007) 3901–3907; P. Setua, D. Seth, N. Sarkar, To probe the structure of methanol and Aerosol OT (AOT) in AOT reverse micelles by FTIR measurements, *Phys. Chem. Chem. Phys.* 11 (2009) 8913–8922.
- [8] J. Kuchlyan, D. Banik, N. Kundu, S. Ghosh, Ch. Banerjee, N. Sarkar, Effect of Confinement on excited-state proton transfer of firefly's chromophore D-luciferin in AOT reverse micelles, *J. Phys. Chem. B* 118 (2014) 3401–3408.
- [9] M.A. Crosio, N.M. Correa, J.J. Silber, R.D. Falcone, A protic ionic liquid when entrapped in cationic reverse micelles, can be used as a suitable solvent for a bimolecular nucleophilic substitution reaction, *Org. Biomol. Chem.* 14 (2016) 3170–3177.
- [10] G.V. Porcal, E.M. Arbeloa, C.A. Chesta, S.G. Bertolotti, C.M. Previtali, Visible light photopolymerization in BHDC reverse micelles. Laser flash photolysis study of the photoinitiating mechanism, *J. Photochem. Photobiol. A Chem.* 257 (2013) 60–65; E.M. Arbeloa, G.V. Porcal, S.G. Bertolotti, C.M. Previtali, Synthesis and characterization of latex nanoparticles using a visible light photoinitiating system in reverse micelles, *Colloid. Polym. Sci.* 293 (2015) 625–632.
- [11] M.A.J. Rodgers, Picosecond fluorescence studies of xanthene dyes in anionic micelles in water and reverse micelles in heptane, *J. Phys. Chem.* 85 (1981) 3372–3374.
- [12] A. Seret, A. Van de Vorst, Solubility properties of Eosin Y and Rose Bengal triplet state in sodium dodecyl sulfate micellar solutions, *J. Phys. Chem.* 94 (1990) 5293–5299.
- [13] B.B. Bhowmik, P. Ganguly, Photophysics of xanthene dyes in surfactant solution, *Spectrochim. Acta A* 61 (2005) 1997–2003.
- [14] M. Chakraborty, A.K. Panda, Spectral behaviour of eosin Y in different solvents and aqueous surfactant media, *Spectrochim. Acta A* 81 (2011) 458–465.
- [15] G.R. Burnett, G.D. Rees, D.C. Steytler, B.H. Robinson, Fluorescence correlation spectroscopy of water-in-oil microemulsions: an application in specific characterisation of droplets containing biomolecules, *Colloids Surf. A* 250 (2004) 171–178; D. Seth, A. Chakraborty, N. Chakraborty, Study of energy transfer from 7-amino coumarin donors to rhodamine 6 G acceptor in non-aqueous reverse micelles, *Chem. Phys. Lett.* 401 (2005) 546–552; S.M.B. Ferreira, Electronic excited-state behavior of Rhodamine 3 B in AOT reverse micelles sensing contact ion pair to solvent separated ion pair interconversion, *J. Phys. Chem. B* 114 (2010) 10417–10426; A. Orte, J.M. Ruedas-Rama, L. Paredes, J.M. Alvarez-Pez, Dynamics of water-in-oil nanoemulsions revealed by fluorescence lifetime correlation spectroscopy, *Langmuir* 27 (2011) 12792–12799.
- [16] E.M. Arbeloa, G.V. Porcal, S.G. Bertolotti, C.M. Previtali, Effect of the interface on the photophysics of eosin-Y in reverse micelles, *J. Photochem. Photobiol. A Chem.* 252 (2013) 31–36.
- [17] M.P. Heitz, F.V. Bright, Rotational reorientation dynamics of xanthene dyes within the interior of Aerosol-OT reversed micelles, *Appl. Spectrosc.* 49 (1995) 20–30.
- [18] S.G. Martínez, O.E. Bertolotti, D.O. Zimermann, S.E. Mártire, N.A. Braslavsky, A kinetic study of the photodynamic properties of the xanthene dye merbromin (mercurochrome) and its aggregates with amino acids in aqueous solution, *J. Photochem. Photobiol. B* 17 (1993) 247–255.
- [19] J.M. Costa-Fernández, A. Sanz-Medel, Air moisture sensing materials based on the room temperature phosphorescence quenching of immobilized mercurochrome, *Anal. Chim. Acta* 407 (2000) 61–69.
- [20] K. Gollnick, T. Franken, M.F.R. Fouda, H.R. Paur, S. Held, Merbromin (mercurochrome) and other xanthene dyes: quantum yields of triplet sensitizer generation and singlet oxygen formation in alcoholic solutions, *J. Photochem. Photobiol. B* 12 (1992) 57–81.
- [21] E. Gurr, Synthetic dyes in biology, Medicine and Chemistry, Academic Press, London, 1971, pp. 193–194.
- [22] A. Jada, J. Lang, R. Zana, R. Makhloufi, E. Hirsch, S.J. Candau, Ternary water in oil microemulsions made of cationic surfactants water, and aromatic solvents. 2. Droplet sizes and interactions and exchange of material between droplets, *J. Phys. Chem.* 94 (1990) 387–395.
- [23] J. Lang, A. Jada, A. Malliaris, Structure and dynamics of water-in-oil droplets stabilized by sodium bis(2-ethylhexyl) sulfosuccinate, *J. Phys. Chem.* 92 (1988) 1946–1953.
- [24] P.G. Seybold, M. Gouterman, J. Callis, Calorimetric: photometric and lifetime determinations of fluorescence yields of fluorescein dyes, *Photochem. Photobiol.* 9 (1969) 229–242.
- [25] H.A. Montejano, M. Gervaldo, S.G. Bertolotti, The excited-states quenching of resazurin and resorufin by p-benzoquinones in polar solvents, *Dyes Pigm.* 64 (2005) 117–124.
- [26] G.R. Fleming, A.W.E. Knight, J.M. Morris, R.J.S. Morrison, G.W. Robinson, Picosecond fluorescence studies of xanthene dyes, *J. Am. Chem. Soc.* 99 (1977) 4306–4311.
- [27] I. Sánchez-Barragán, J.M. Costa-Fernández, A. Sanz-Medel, Tailoring the pH response range of fluorescent-based pH sensing phases by sol-gel surfactants co-immobilization, *Sens. Actuators B* 107 (2005) 69–76.
- [28] J. Chrysochoos, L.I. Ovadia, Pulse radiolysis of aqueous eosin, *J. Phys. Chem.* 71 (1967) 1629–1636; Y. Tachikawa, K. Kobori, A. Akiyama, U.E. Katsuki, S. Steiner, Spin dynamics and zero-field splitting constants of the triplet exciplex generated by photoinduced electron transfer reaction between erythrosin B and duroquinone, *Chem. Phys. Lett.* 360 (2002) 13–21.
- [29] J.P. Fouassier, Photoinitiation Photopolymerization and Photocuring, Hanser Publishers, Munich, New York, 1995; J.P. Fouassier (Ed.), Photochemistry and UV curing: New trends, Research Signpost, Trivandrum, 2006.
- [30] M.V. Encinas, A.M. Ruffs, S.G. Bertolotti, C.M. Previtali, Xanthene dyes/amine as photoinitiators of radical polymerization: a comparative and photochemical study in aqueous medium, *Polymer* 50 (2009) 2762–2767.
- [31] E.M. Arbeloa, G.V. Porcal, S.G. Bertolotti, C.M. Previtali, Synthesis and characterization of latex nanoparticles using a visible light photoinitiating system in reverse micelles, *Colloid Polym. Sci.* 293 (2015) 625–632.
- [32] Ian R. Gould, Deepak Shukla, David Giesen, Samir Farid, David Giesen and Samir farid, energetics of electron-Transfer reactions of photoinitiated polymerization: dye-Sensitized fragmentation of N-Alkoxy pyridinium salts, *Helv. Chim. Acta* 84 (2001) 2796–2812.
- [33] T. Shida, Electronic Absorption Spectra of Radical Ions, Elsevier, Amsterdam, 1988.
- [34] G. Porcal, S.G. Bertolotti, C.M. Previtali, M.V. Encinas, Electron transfer quenching of singlet and triplet excited states of flavins and lumichrome by aromatic and aliphatic amines, *Phys. Chem. Chem. Phys.* 5 (2003) 4123–4128.
- [35] H. Kim, N. Kitamura, Y. Kawanishi, S. Tazuke, Photoinduced electron transfer reactions of ruthenium(II) complexes 2. Oxidative quenching of excited tris (2,2'-bipyridine)ruthenium(2+) by neutral organic electron acceptors, *J. Phys. Chem.* 93 (1989) 5757–5764.