Journal of Photochemistry and Photobiology A: Chemistry 310 (2015) 165–170

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

Photoionization processes of charged pyrene derivatives in reverse micelles. The effect of the interfacial charge

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ARTICLE INFO

Article history:
Received 26 March 2015
Received in revised form 24 April 2015
Accepted 18 May 2015
Available online 21 May 2015

Keywords:
Reverse micelles
AOT
BHDC
Photoionization
Pyrene derivatives
Laser photolysis

ABSTRACT

The laser flash photolysis studies of (4-(1-pyrenyl)butyl)trimethylammonium bromide (PBTMA) and 1-pyrene sulfonic acid (PSA) were carried out in BHDC and AOT reverse micellar solutions in benzene. At low laser intensities only the triplet state was observed as a transient species and the photophysical properties of the probes are very similar in both systems. Notable differences arise at high laser intensities. Under these conditions a photoionization process is observed in BHDC for both probes, as is apparent by the presence of the radical cation of the pyrenyl group. Hydrated electrons are not observed at times longer than 100 ns. On the other hand the photoionization process is not detected in AOT. However, a slight photoionization may be induced in AOT by the presence of benzyl alcohol. These results are interpreted by the different ability of AOT and BHDC to interact with the geminate radical–electron pair.

1. Introduction

The investigation of charge transfer processes in organized media is of great concern due to the potential employment of these reactions in the production of energy rich species [1,2]. In particular, reverse micelles can act as microreactors with specific effects on the generation of reactive species by photoinduced electron transfer processes [3,4]. Therefore, it is of interest to investigate the factors that govern the kinetics and product distribution of photochemical charge transfer reactions in reverse micellar systems.

The dramatic changes observed for a given reaction, as compared with homogeneous solvents, can be explained by the physical properties of the interfacial region of the organized system. Of particular interest are the excited state electron transfer reactions of molecules anchored to the interface. Previously we reported the electron transfer quenching of charged pyrene derivatives in AOT (sodium bis(2-ethylhexyl) sulfosuccinate) reverse micelles (RMs) [5] and the charge separation in the pyrene-dimethylaniline exciplex in positive benzylhexadecyldimethyl-ammonium chloride (BHDC) RMs [6]. The results were explained in terms of the local micropolarity and viscosity of the interface. More recently the electron transfer quenching of the triplet state dyes by amines in RMs was published by us [7]. It was found that the quenching process for amines incorporated to the RMs was much more effective than in homogeneous solvents. While similar quantum yields for the charge separation process were attained with a concentration ten times lower in the amine for a cationic dye (safranine) in AOT RMs, the quantum yields were much lower for an anionic dye (eosin).

Although aqueous photoionization have not been always considered in the context of the Marcus theory of electron transfer, the theory provides a framework in which to analyze photoionization as an electron-transfer process. In this framework, the transfer is from an excited donor to a solvation environment that accepts the photoejected electron [8]. Photoionization of several probes in direct and reverse micelles was widely investigated [9–11]. In cationic direct micelles the major photophysical process after laser excitation was the triplet formation [9], while in anionic micelles photoionization was observed to proceed efficiently [9]. On the other hand, in reverse micelles the photoionization of tetramethyl-benzidine is more efficient in cationic (BHDC) than in anionic (AOT) micelles [11].

The photophysical properties of pyrene and its charged derivatives in normal and reverse micelles have been the subject of a large number of papers. It is well known that laser excitation of these molecules, in low polarity solvents like cyclohexane and *n*-hexane, leads mainly to the pyrene excited triplet. However, in protic and aprotic polar solvents like methanol, water and acetonitrile, photoionization is observed [12,13]. This process was also observed in direct micelles [14,15], lipid bilayers [16], zeolites [17] and in reverse micellar solutions [13]. In particular,

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http://dx.doi.org/10.1016/j.jphotochem.2015.05.020
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when pyrene butyric, pyrene dodecanoic or pyrene sulfonic acid (PSA) are laser pulse irradiated in AOT/heptane/water reverse micelles it is possible to observe the cation of pyrene together with the excited singlet and triplet states [13,18,19]. On the other hand, the laser flash excitation of pyrene itself in the same medium, affords only the excited triplet as a long lived transient species [20].

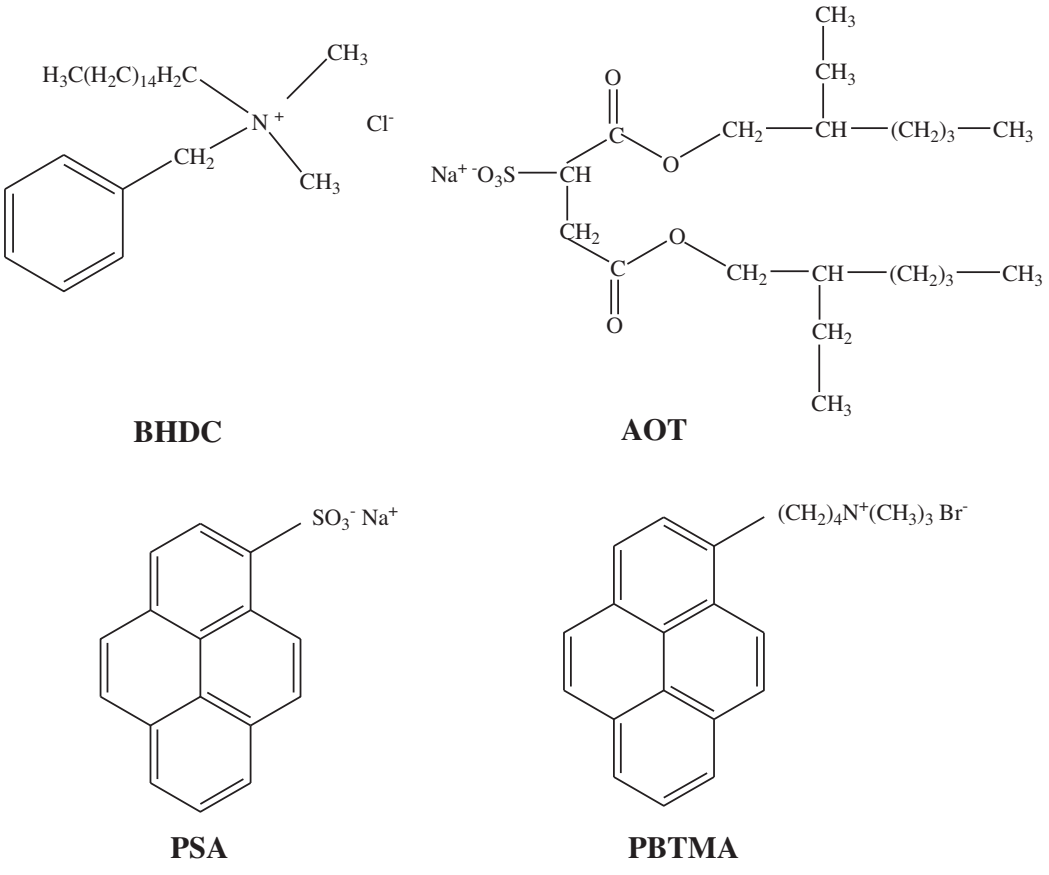
In spite of the great number of papers on the excited states of pyrene and its derivatives, the effect of the interface on the photoionization of these probes in reverse micellar systems has not been investigated. The comparison of the effect of headgroup charge on the location and penetration depth in the interface of charged probes is of great concern for the potential used of RMs as nano-reactors in a variety of situations [21]. To our knowledge there is not a comparative study of the photophysical processes of pyrene derivatives in cationic and anionic reverse micelles. The photoionization of PSA, pyrene tetrasulfonic acid sodium salt (Na_4PS_4) and pyrenebutyric acid has been the subject of a detailed study by Mori et al. in aqueous solution [22] and in AOT/isooctane reverse micelles [23]. The laser photolysis of PSA and Na_4PS_4 under two photon photoionization conditions was later on study by the same authors [24]. The photoproducts as well as their yields was determined under a variety of conditions and their origin was the ulterior reactions of the primarily formed cation radical of the pyrene derivative.

BHDC is a cationic surfactant that has the ability of solubilize relatively large amounts of water in benzene, producing transparent microemulsions. AOT also forms reverse micelles in benzene. Therefore, a study of the influence of the charge of the surfactant's head groups on the excited states and photoionization yields may be attempted in benzene as a common bulk organic solvent. When AOT is dissolved in benzene, it forms microemulsions which are optically transparent and stable upon the addition of water until a molar water to AOT ratio (w) of 12 [25]. In the same solvent BHDC forms stable reversed micelles up to $w = 25$. In the present study we wish to report about the quantum yields of excited state processes of pyrene derivatives in cationic (BHDC) compared to anionic (AOT) reverse micelles, in the same bulk organic solvent. The cationic probe 4-(1-pyrenyl)butyl)trimethylammonium bromide (PBTMA) and the anionic 1-pyrene sulfonic acid sodium salt (PSA) were chosen for the study. It will be shown that while fluorescence and triplet yields are very similar in both media, large differences are observed in the photoionization yield. See Scheme 1 for the structures of surfactants and probes.

2. Materials and methods

BHDC (Sigma Chem. Co.) was recrystallized several times from ethylacetate and dried under vacuum. AOT (Sigma Chem. Co.) was dried under vacuum and used without further purification. PBTMA and PSA were products from Molecular Probes and employed as received. Benzene (Sintorgan spectroscopic grade) was dried before use.

The set-up for transient absorption experiments consisted of a Nd-YAG laser (Spectron Laser Systems, SL 404). The third harmonic at 355 nm was used for the excitation. The laser beam was defocused and directed at right angles to the analyzing beam from a Xenon arc lamp. The detection system comprises a f/4 monochromator and a red extended photomultiplier (Hamamatsu R666 or RCA 4840). Transients' signals were acquired and averaged by a Hewlett-Packard 54504A digitizing oscilloscope and transferred through to a PC computer for processing. Most of the



Scheme 1. Structures of surfactants and probes.

experiments were performed in 10^{-5} M degassed solutions of the pyrene derivative at laser energies of from 1 to 25 mJ/pulse.

The experiments for determination of triplet state quantum yields were performed with a nitrogen laser (Laseroptics) or with the Nd-YAG laser at energies lower than 5 mJ per pulse. Triplet quantum yield were determined relative to ZnTPP in benzene ($\Phi_T = 0.83$; $\varepsilon_T = 73{,}000\ M^{-1}\ cm^{-1}$ at 470 nm) [26]. The extinction coefficient of the triplet sate of PSA and PBTMA was taken the same as that of pyrene in polar solvents ($\varepsilon_T = 30{,}400\ M^{-1}\ cm^{-1}$) [27].

Fluorescence spectra were measured with a Spex Fluoromax spectrofluorometer. The quantum yields were determined with a standard of anthracene in ethanol ($\Phi_F = 0.27 \pm 0.03$) [27]. Refractive index correction was applied considering the refraction index of the reverse micellar solution the same as that of benzene. The water content of the solutions was expressed as the ratio $w = [H_2O]/[\text{surfactant}]$.

3. Results

3.1. PSA (1-pyrene sulfonic acid sodium salt) photoionization

When AOT is dissolved in benzene, it forms microemulsions which are optically transparent and stable upon the addition of water until a w value of 12. Beyond this the solution is optically opaque. In the same solvent BHDC forms stable reversed micelles up to $w = 25$. In AOT/heptane RMs PSA is believed to be located mainly at the interface [19,28] although it bears the same charge as the detergent molecules. It is most probably co-micellizing with the surfactant molecules. It was reported that, in alkane bulk organic solvent, at $w > 10$ PSA starts to move to the water pool and that ca. 20% is in the water pool at $w = 30$, [19]. Quenching experiments by indolic compounds in AOT RMs [5] show that the behavior of PSA is very similar to that observed for (1-pyrenyl) methyl trimethylammonium iodide, which is a positive probe assumed to be totally incorporated into the AOT interface. In the BHDC RMs PSA is anchored to the positive interface.

The photophysical properties of PSA in AOT/benzene and BHDC/benzene reverse micellar solutions were measured as described in the Materials and methods section. The fluorescence spectrum of 1.0×10^{-4} M PSA in water (excitation = 357 nm) shows emission bands at 376 and 394 nm. When the PSA concentration is increased 50-fold to 5.0×10^{-3} M excimer emission appears at 490 nm [29]. The fluorescence quantum yield was determined as 0.47 [13]. In RMs the spectrum is very similar to that in water. Excimer emission was not observed at the concentrations employed. In Table 1 the fluorescence and triplet quantum yields obtained at low laser fluence (less than 5 mJ per pulse, 337 or 355 nm) are presented. It can be seen that their sum is close to one within the experimental error. Under these conditions, the only transient species observed in the microsecond time scale was the triplet state in all media. Values of the quantum yields were practically insensitive to changes in the water content.

When PSA is excited at 355 nm at higher fluence (25 mJ) the transient absorption spectrum in water in the microsecond region presents two main bands at 415 nm (T–T) and 460 nm (radical cation) [13]. A third band at 490 nm can be ascribed to the radical anion formed by the fast capture of hydrated electrons by PSA [22]. In the short time 0–500 ns a strong absorption in the region 600–800 nm corresponding hydrated electrons was observed [22]. On the other hand, excitation of PSA at 355 nm with laser fluence of 25 mJ in reverse micellar solutions of AOT/benzene at $w = 10$ results in a transient spectrum showing two main bands at 420 and 520 nm which can be assigned to the T–T absorption [30],Fig. 1. The absence of a strong absorption of the radical cation around 460 nm and the radical anion at 490 is notable.

Otherwise, in BHDC/benzene solutions the absorption of the radical cation at 460 nm can clearly be seen in Fig. 1, but not the large amount of radical anion present in homogeneous water solution. Very short lived weak electron absorption at 700 nm could also be detected. The presence of a shoulder at 490 nm indicates a small amount of the radical anion. This observation confirms the operation of a photoionization process. The electron capture by the BHDC molecules in the palisade where PSA localizes can explain the very small absorption at 490 nm and the feeble short lived electron absorption as compared with water.

In Fig. 2 the time profile of the transient absorption of PSA at two wavelengths are shown in water and in BHDC/benzene solution at $w = 10$. It can be seen that in homogeneous solution the triplet decay, monitored at 425 nm, is much faster and the photoionization yield, as measured by the radical cation absorption at 460 nm, is higher.

3.1.1. PBTMA (4-(1-pyrenyl)butyl)trimethylammonium bromide) photoionization

In AOT/benzene RMs the positive probe PBTMA can be considered to be totally bound to the micellar interface. In pure benzene it is almost insoluble. It readily dissolves in the presence of AOT or BHDC and becomes strongly fluorescent. In AOT RMs the fluorescence decay time could be fitted by a single exponential at all the AOT concentrations and w values studied. Its absorption and emission spectra were similar to those observed in solutions of AOT in alkane solvents. This means that the excited probe molecules constitute a single and homogeneous population bound to the negative interface. In BHDC the probe is mainly localized in the interface comicellizing with the cationic surfactant due to its amphiphillic character. Photophysical parameters of the probe in reverse micelles at low laser pulse energy are also collected in Table 1. Here again the sum of fluorescence and triplet quantum yield is close to unity. Also in this case the values were practically independent of the water content.

At low laser fluence at 337 or 355 nm the only transient species observed is the triplet state in AOT and BHDC RMs. At higher laser intensity at 355 nm in BHDC a strong absorption at 460 nm can be seen, Fig. 3, which can be ascribed to the radical cation of PBTMA by comparison with other pyrene derivatives [30,31].

In Fig. 4 the transient spectra in water, AOT and BHDC with the same ground state absorption and laser intensity are compared.

Table 1
Fluorescence and triplet state quantum yields of PBTMA and PSA in reverse micellar solutions at 25 °C. Solvent benzene, $w = 10$. Surfactant concentration 0.1 M.

	PBTMA		PSA	
	Φ_F[a]	Φ_T[b]	Φ_F[a]	Φ_T[b]
BHDC	0.74	0.20	0.84	0.11
AOT	0.78	0.12	0.93	0.10

[a] Fluorescence quantum yields, estimated errors ± 10%.
[b] Triplet state quantum yields, estimated errors ± 20%.

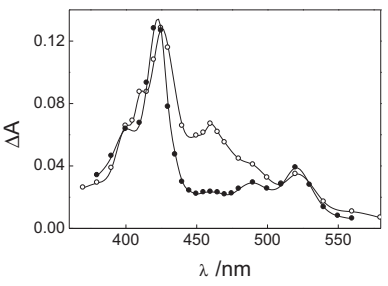


Fig. 1. Transient absorption spectrum of PSA in AOT/benzene $w = 10$ at 10 μs after the laser pulse (●) and in BHDC/benzene $w = 10$ at 4 μs after the laser pulse (○).

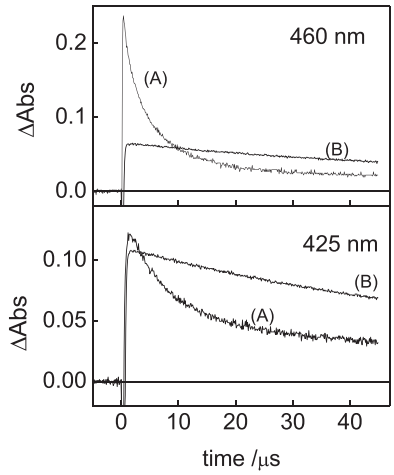


Fig. 2. Decay of the transient absorption of PSA in water (A) and BHDC, w = 10 (B)

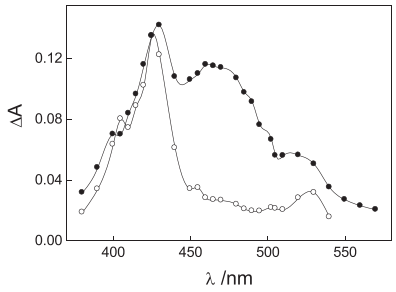


Fig. 3. Transient absorption spectra of PBTMA in BHDC/benzene solution at 0.1 M surfactant and $w = 10$ taken at 10 μs after the laser pulse. (●) λ_{exc} 355 nm laser intensisty = 25 mJ; (○) λ_{exc} 337 nm, laser intensity = 2 mJ.

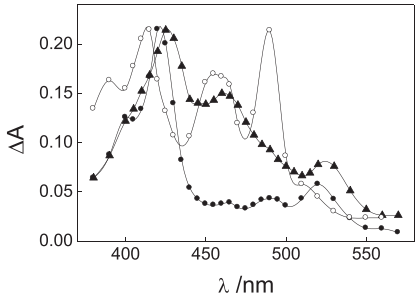


Fig. 4. Normalized transient absorption spectrum of PBTMA in water (○), BHDC (▲) and AOT (●) taken at 5 μs after the laser pulse at 355 nm.

The lack of photoionization in AOT and absence of the radical anion absorption at 490 nm in BHDC are important features.

In Fig. 5 the decay of the T–T absorption at 420 nm and that of the radical cation of PBTMA at 460 nm are shown in water and in BHDC/benzene solution at $w = 10$. Here again the transient species are much longer lived in the reverse micellar medium while the triplet and the photoionization yield are higher in water. In water both the triplet and the radical anion decay by mixed first and second order kinetics. In the case of the triplet state it is due to the contribution of a T–T annihilation process. The radical cation on the other hand decays by a first order process by reaction with the ground state to a long lived transient species. In the RMs the second order mechanisms are precluded by the compartmentalization and low occupation number. This results in a longer lived triplet and radical cation in the RMs.

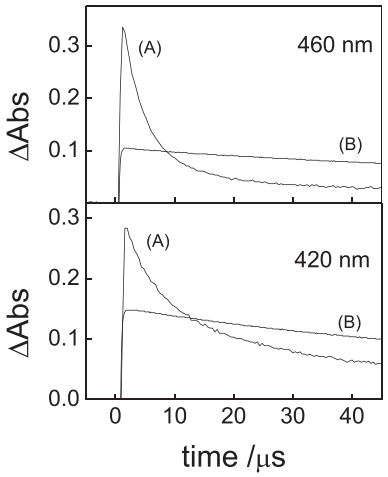


Fig. 5. Decay of the transient absorption of PBTMA in water (A) and BHDC, $w = 10$ (B).

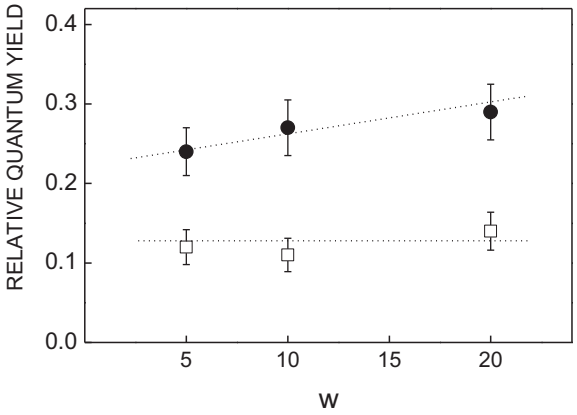


Fig. 6. Relative photoionization quantum yield in BHDC/benzene reverse micelles as a function of the water content (□) PSA; (●) PBTMA.

In Fig. 6 the effect of the size of the water pool on the photoionization yield in BHDC RMs is presented. It can be seen that while for PSA the yield is practically independent of the water content for the positive probe it increases with w.

4. Discussion

Both probes present a similar behavior under laser excitation in RMs in spite of the different charge. The most remarkable finding of this study is the lack of photoionization in AOT/benzene solutions, contrasting with previous reports in the literature [11,32]. Photoionization of PSA, and other negatively charged pyrenyl probes, was reported in AOT/*n*-alkane/water reverse micelles [18,19,22,23]. The radical cation of the pyrenyl group and the hydrated electron were identified from its absorption spectra following laser flash excitation. For the hydrated electron the observed lifetime in these microemulsions was less than 100 ns [33]. On the other hand the pyrene radical ion was very much long lived. It seems that changing the organic solvent from an *n*-alkane to benzene precludes the observation of the charge separation process in AOT microemulsions. On the other hand, radical cations of both probes are detected in BHDC/benzene. Since the photophysical parameters determined at low laser intensity are very similar for the two probes in both reverse micellar systems, it can be concluded that the variance in photoionization yield is not due to differences in the interaction of the excited probes with the

surfactant molecules. With regard to the location of the probes it may be presumed that, due to electrostatic and hydrophobic interactions, they reside mainly in the interfacial region between the organic solvent and the water pool [28,34,35].

The contrasted behaviors of both reverse micellar systems most likely arise in the different interaction of the surfactants with the geminate radical–electron pair. BHDC is probably trapping electrons much more efficiently than AOT or the water pools. Since the pyrenyl groups of the probes are situated in the less polar region of the interface, toward the organic phase, the photoejected electrons may be considered as "dry" electrons. The large differences in the photoionization yield of pyrene derivatives in BHDC/benzene/water relative to AOT/benzene/water reverse micelles can be explained if it is assumed that dry electrons react with the surfactant's polar heads with rate constants similar to hydrated electrons. It is known that the benzyltrimethyl-ammonium ion, a model compound for BHDC, is a very good acceptor of solvated electrons with a rate constant of $1.2 \times 10^{10}\,M^{-1}\,s^{-1}$ [36]. The reaction induces the decomposition of the ammonium ion giving benzyl radicals and triethylamine [36]. On the other hand succinate ions, the model for AOT, are not as efficient as benzyltrimethyl-ammonium ion in capturing solvated electrons. In this case the rate constant is $2.4 \times 10^{7}\,M^{-1}\,s^{-1}$ [36]. If a similar reactivity is supposed for the electron in the reverse micelles interface it may be concluded that BHDC will capture electrons from the geminate pair more rapidly than AOT leading to the observed results. This supposition can also explain the no observation of the solvated electron absorption band.

An alternative explanation may be the effect of a different location of the anionic probes. In AOT/isooctane reverse micelles it was proposed that PSA is partitioned between the interface and the water pool [19]. Thus, photoionization in alkane solvents may be explained by a higher exposure of the probes to an aqueous environment. However, this is not consistent with the lack of effect of the water content on the photionization yield shown in Fig. 6. In the case of PBTMA a slight increase of the yield with *w* can be seen. It may be related to the change in the curvature of the interface that makes the pyrenyl group of PBTMA sense a more polar environment, this is most probably due to some water molecules penetrating into the micellar interface.

That the photoionization process is predominately controlled by the interface's properties is further evidenced by the effect of benzyl alcohol. The results of Fig. 7 show that the presence of benzyl alcohol induces a slight extent of photoionization in AOT/benzene micelles. It is known that benzyl alcohol increases the rate of exchange of material between AOT reversed micelles [37] because it causes a disruption of the alignment of the surfactant's head groups at the interface. Benzyl alcohol also increases the water–AOT interfacial area [38] and changes the size of AOT/alkane reversed micelles making the curvature of the surfactant shell less convex to the oil. Because of these effects, it probably increases the rate of electron capture by the water pools. In this way the presence of benzyl alcohol may induce a small amount of photoionization of PBTMA by decreasing the back recombination of the radical ion–electron pairs.

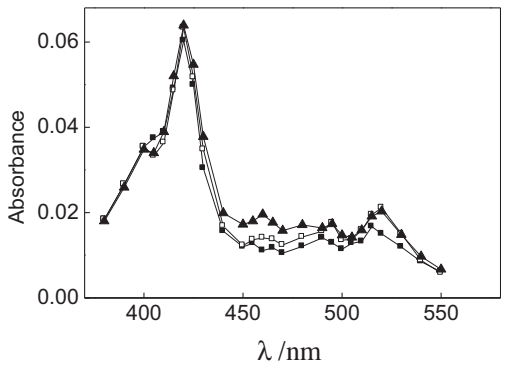


Fig. 7. Transient absorption spectrum of PBTMA in AOT/benzene w = 10 in the absence (■) and in the presence of benzyl alcohol 0.1 M (□); 0.3 M (▲).

In summary, while the photophysical properties of the probes PBTMA and PSA are very similar in reversed micellar solutions of BHDC and AOT disperse in benzene, notable differences arise in the photoionization processes. In BHDC at high intensity laser irradiation both probes photoionize while this process is absent in AOT/benzene micelles. These results are interpreted by the different ability of AOT and BHDC to interact with the geminate radical-electron pair.

Acknowledgments

Financial support from CONICET (PIP 2010-0284) and Universidad Nacional de Río Cuarto is gratefully acknowledged.

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