



Contents lists available at ScienceDirect

# Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: [www.elsevier.com/locate/jphotochem](http://www.elsevier.com/locate/jphotochem)

## Photophysics of thionine in AOT and BHDC reverse micelles. Quenching of the triplet state by aliphatic amines studied by transient absorption spectroscopy



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

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

## ARTICLE INFO

## Article history:

Received 13 March 2017

Received in revised form 30 May 2017

Accepted 5 June 2017

Available online 7 June 2017

## Keywords:

Thionine

Photophysics

State triplet

Reverse micelles

## ABSTRACT

The photophysics of thionine (3,7-diamino-5-phenothiazinium) ( $\text{Th}^+$ ) was investigated in reverse micelles (RMs) of sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and benzyldimethylhexadecylammonium chloride (BHDC) with special emphasis on the triplet state processes. In RMs both the absorption and emission spectra of the dye present a red shift with respect to pure water. The absorption maximum wavelength and Stokes shift show a tendency towards the values in water, although do not reach them even with the higher water content examined. The photophysical parameters are more affected by the water content in BHDC than in AOT. The triplet state of  $\text{Th}^+$  was investigated by the technique of laser flash photolysis. The T-T absorption spectrum presents a strong absorption band in the region between 770 and 800 nm, corresponding to the monoprotonated triplet form of the dye. This spectrum is red shifted with respect to water in the RMs. The triplet quenching by aliphatic amines was investigated. The triplet decay is well fitted by a bi-exponential function in the presence of the hydro-soluble triethanolamine (TEOA) in both RMs. This behavior is interpreted as the result of a very fast intramicellar quenching, followed by slow process that may be ascribed to an intermicellar exchange of amine molecules between RMs. The kinetic analysis showed that intermicellar exchange rate constant is two orders of magnitude more effective in BHDC than in AOT. Meanwhile, in the quenching by the hydrophobic tributylamine (TBA) the decay is mono-exponential. The amine is located preferentially in the bulk organic phase and the quenching mechanism involves the interaction of the amine with the monoprotonated triplet of dye reaching in the micellar interface. It is interesting to note that the apparent quenching rate constant by TBA is one order of magnitude lower than the exchange rate constant by TEOA.

© 2017 Elsevier B.V. All rights reserved.

### 1. Introduction

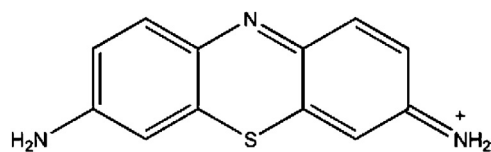
In the last years, there has been increasing interest in the reverse micelles (RMs) and microemulsions primarily because of the large diversity the microenvironments that these materials provide. RMs are thermodynamically stable dispersions of an organic solvent and water stabilized by a surfactant and in many cases a cosurfactant is necessary. A surfactant monolayer is oriented in such a manner that its tails are directed toward nonpolar solvent and the polar head-groups enclose the aqueous droplet size of nanometers (water pool). The average size of such RMs is dependent on the amount of solubilized water and can be expressed as the water to surfactant molar ratio,  $w = [\text{H}_2\text{O}]/[\text{Surf}]$

[1]. The state of water in the aqueous pool of RMs is different from that of bulk water and depends significantly on the distance from the surfactant interface. Properties such as polarity, viscosity, pH and the organized states of the interfacial and bulk water are quite different. Several molecular probes have been used to characterize the properties of the diverse microenvironment in RMs [2]. Most of these studies are based on changes in the photophysical properties as well as the reactivity of the excited states of synthetic dyes compartmentalized in these media and their dependence on the parameter  $w$ . The reverse micelles (RMs) have found a wide range of applications in the fields of chemistry, as the biology and technology [3,4]. Currently they are being widely used as a means of synthesis for obtaining different particles [5].

Thionine (3,7-diamino-5-phenothiazinium) ( $\text{Th}^+$ , Scheme 1) is a cationic phenothiazine dye that has been widely studied due to their interesting physicochemical properties [6,7]. It has been employed as a photosensitizer in photogalvanic studies [8],

\* Corresponding authors.

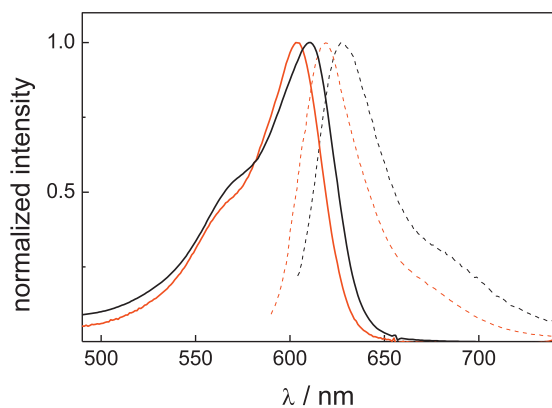
E-mail addresses: [gporcal@exa.unrc.edu.ar](mailto:gporcal@exa.unrc.edu.ar) (G.V. Porcal), [cprevitali@exa.unrc.edu.ar](mailto:cprevitali@exa.unrc.edu.ar) (C.M. Previtali).

Thionine (Th<sup>+</sup>)

**Scheme 1.** Molecular structure of the dye employing.

photodynamic therapy [9] and as photoinitiator of vinyl polymerization [10]. It has been reported that Th<sup>+</sup> interacts with DNA as evidenced by strong hypsochromic and bathochromic effects on the absorption and fluorescence spectra and quenching of fluorescence [11]. Several papers describe the photophysical properties of this dye in organized media. Basu et al. [12] investigated the photophysical behavior of Th<sup>+</sup> in different solvents and liposomes of phosphatidylcholine, they found that the dye is located at the liposome-water interface. Bhowmik and Mukhopadhyay performed photophysical studies of the dye in the presence of triton X-100 [13], it was found that the dye forms a charge-transfer complex with the surfactant. In aqueous solution, the dye presents a concentration-dependent absorption spectrum due to the presence of aggregates. This aggregation is also influenced by the pH [6,14].

Our group has been studying the photophysics and photochemistry of dyes in both aqueous and microheterogeneous media for more than a decade [15–19]. In previous works, we published a study on the photophysics of safranin, a cationic dye, in AOT (sodium bis(2-ethylhexyl)sulfosuccinate) and BHDC (benzyltrimethylhexadecylammonium chloride) reverse micelles [18,19]. In these systems, the triplet state of the dye has a longer lifetime than in homogeneous solvents. We conclude that this result is due to compartmentalization effect that suppresses the self-quenching process. In addition, we have characterized the properties of the excited states of eosin, an anionic dye, in the same micellar systems where it was found the dye localizes in the interface of the reverse micelles in both AOT and BHDC. The main difference found is that in AOT the photophysics parameters are sensitive to the size of the water pool [15]. Most reports on Th<sup>+</sup> photophysics describe studies involving the singlet-excited state. To the best of our knowledge, the properties of the triplet state of the dye in reverse micelles have been scarcely explored. This aspect is important since the triplet is the responsible for many useful applications of the dyes, one of the most important being its use as photoinitiator of the vinyl polymerization.



**Fig. 1.** Absorption and fluorescence emission spectra of Th<sup>+</sup> ( $5 \times 10^{-6}$  M) in AOT 0.2 M/n-heptane/water at  $w = 10$  (red) and BHDC 0.1 M/toluene/water at  $w = 10$  (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

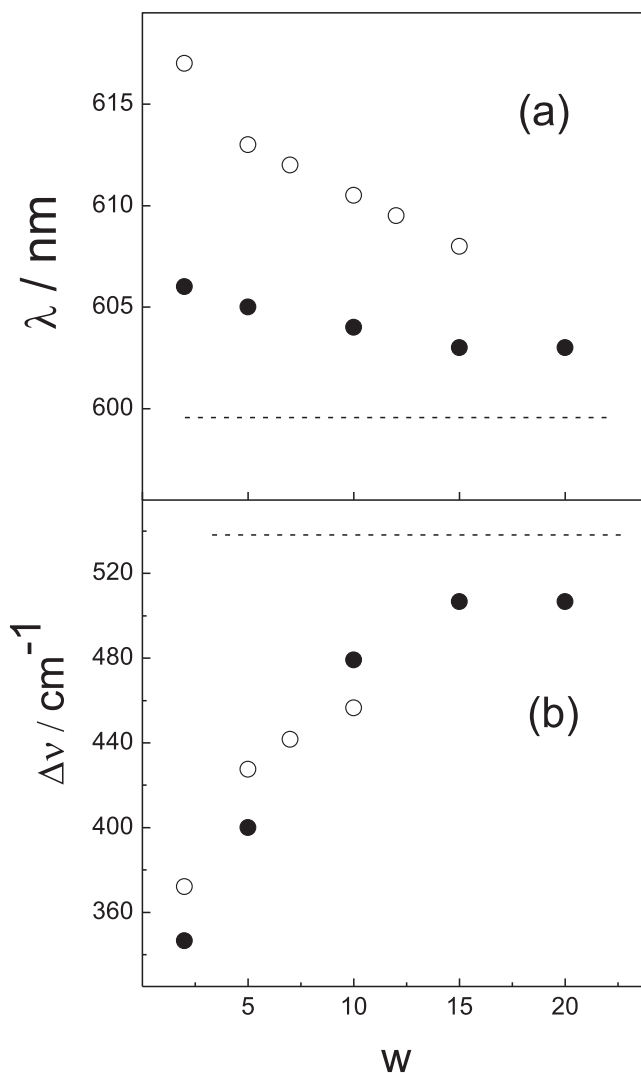
**Table 1**

Absorption and fluorescence maximum ( $\lambda_{\max}$ ) of thionine ( $5 \times 10^{-6}$  M) in homogeneous and reverse micelles media.

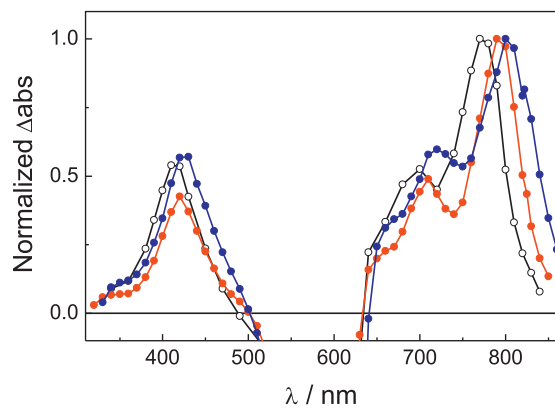
medium	$\lambda_{\max}$ (abs)/nm	$\lambda_{\max}$ (fl)/nm
water	599	620
MeOH	600	620
AOT/heptane/ water $w = 10$	603	623
BHDC/toluene/ water $w = 10$	610	628

In this paper, we have focused on the photophysics of the dye Th<sup>+</sup> in confined media with an emphasis on the study of the properties of the triplet state. In particular, the effect of different interfaces on the quenching processes of the triplet state by aliphatic amines, was investigated. The anionic surfactant AOT and the cationic surfactant BHDC, were employed. Both surfactants form RMs stables without the aid of a co-surfactant.

The absorption and fluorescence emission spectra of Th<sup>+</sup> 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. Laser flash photolysis studies have been performed to identify the different



**Fig. 2.** (a) Absorption maximum wavelength of Th<sup>+</sup> ( $5 \times 10^{-6}$  M) in BHDC/toluene RM at (○) and in AOT/heptane (●) and (b) Stokes shift, as a function of the size of the water pool. The dotted lines correspond to the values in bulk water.



**Fig. 3.** Transient absorption spectra of  $\text{Th}^+$  ( $3 \times 10^{-5} \text{ M}$ ) taken immediately after the laser pulse in buffer pH 8 (black); in AOT at  $w = 10$  (red) and in BHDC at  $w = 10$  (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

transient species of the dye and the mechanism of interaction with aliphatic amines as electron donors.

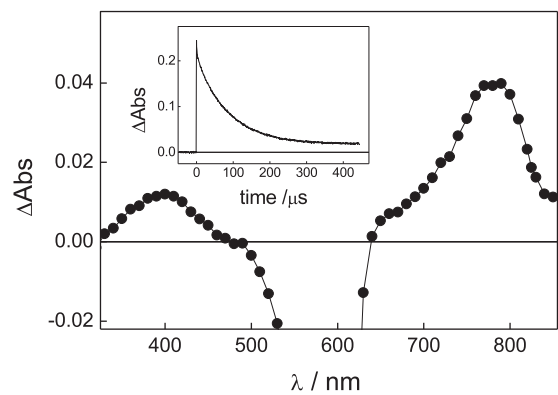
## 2. Experimental

### 2.1. Materials and methods

Thionine (3,7-diamino-5-phenothiazinium) ( $\text{Th}^+$ ) supplied by Sigma was recrystallized from ethanol-water. AOT from Aldrich was dried under vacuum over  $\text{P}_2\text{O}_5$ . BHDC from Sigma was twice recrystallized from ethyl acetate and dried under vacuum. The solvents, *n*-heptane and toluene were from Sintorgan (HPLC grade) and used as received. Water was purified through a Millipore Milli-Q system. Reverse micelles solutions were prepared by dissolving the surfactant in the organic solvent, *n*-heptane for AOT and toluene in the case of BHDC. A small amount of  $\text{Th}^+$  dissolved in water was added to these micellar solutions, so that the final total analytical concentration of the dye was  $5 \times 10^{-6} \text{ M}$  and  $3 \times 10^{-5} \text{ M}$  for the experiences of the singlet and triplet state respectively. The micellar water content,  $w = [\text{H}_2\text{O}]/[\text{Surfactant}]$ , was adjusted by adding pure water up to desired ratio. The surfactant concentration was kept constant at 0.2 M for AOT and 0.1 M for BHDC. It is not possible to work at  $w > 15$  in BHDC because at room temperature the solutions become cloudy. According to the reported surfactant aggregation numbers for the formation of RMs [20,21], we obtain the mean occupation number of the dye is  $\leq 0.01$  in AOT, while in BHDC it is  $\leq 0.03$ . Therefore, the probability of localization of more than one  $\text{Th}^+$  molecules per micellar aggregate is neglected. Triethanolamine (TEOA) and tributylamine (TBA) both from Aldrich, were purified by vacuum distillation before use. In the quenching experiments, small aliquots of a concentrated aqueous solution of TEOA were added to the RMs. In the case of TBA the amine was added as the pure compound.

**Table 2**  
T–T absorption bands of thionine in different media.

medium	$\lambda_1$ (nm)	$\lambda_2$ (nm)	$\lambda_3$ (nm)
water	770	700	410
MeOH	780	700	420
AOT/heptane/ water $w = 2$	800	720	420
AOT/heptane/ water $w = 10$	790	710	420
BHDC/toluene/ water $w = 2$	810	725	430
BHDC/toluene/ water $w = 10$	800	720	425



**Fig. 4.** Long time absorption spectrum of  $\text{Th}^+$  ( $3 \times 10^{-5} \text{ M}$ ) in AOT at  $w = 10$  taken at 400  $\mu\text{s}$  after the laser pulse. Inset: T–T absorption decay at 800 nm.

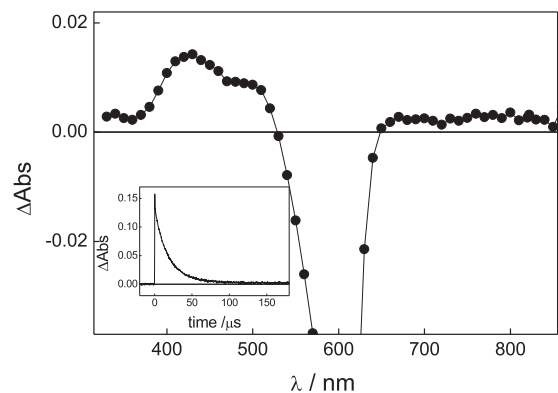
The absorption spectra were obtained by using a Hewlett Packard 6453E diode array spectrophotometer. Fluorescence spectra were measured with a Spex Fluoromax spectrofluorometer in air-equilibrated solutions. Transient absorption measurements were carried-out by excitation at 532 nm using a laser flash photolysis equipment as previously described [22]. The samples were deoxygenated by bubbling during 15 min with organic solvent-saturated high purity argon. All experiments were performed at 25 °C or 32 °C for the reverse micelles of AOT and BHDC respectively.

## 3. Results and discussion

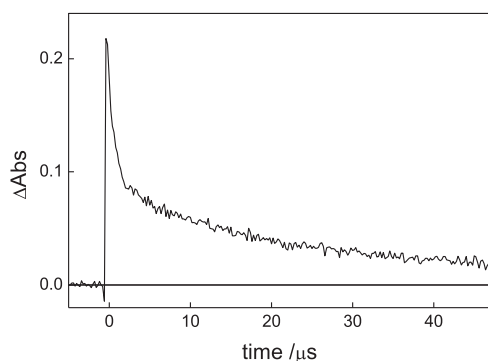
In dilute aqueous or methanolic solutions, thionine presents a strong absorption at ca. 600 nm with a maximum absorption coefficient close to  $5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ , which is red shifted when the solvent polarity decreases. This absorption band has been assigned to the monomer of the dye with a positive charge. A shoulder at 560 nm is also present in dilute solutions attributed to  $1 \leftarrow 0$  vibronic transition [23].

The absorption and fluorescence emission spectra of the dye in RMs are shown in Fig. 1 and a summary of the maximum wavelength in different media is presented in Table 1.

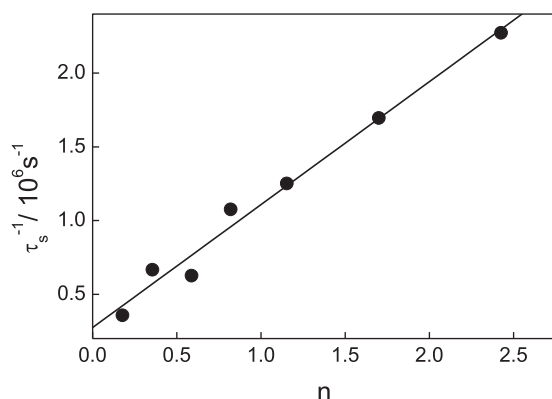
Thionine presents a  $\text{pK}_a$  around 8, the monocationic species is predominant at  $\text{pH} < 8$  with an absorption band peaked at 599 nm. At higher pH a new band is present at 510 nm that is attributed to the neutral conjugated base of the dye [6]. The absorption spectrum in both AOT and BHDC corresponds to the monocation, as expected from the buffer like effect of the RMs [24] on the water pool where the dye would be located. The presence of dimers and higher aggregates of the dye may also be disregarded, since at the



**Fig. 5.** Long time absorption spectrum of  $\text{Th}^+$  ( $3 \times 10^{-5} \text{ M}$ ) in BHDC at  $w = 10$  taken at 100  $\mu\text{s}$  after the laser pulse. Inset: T–T absorption decay at 800 nm.



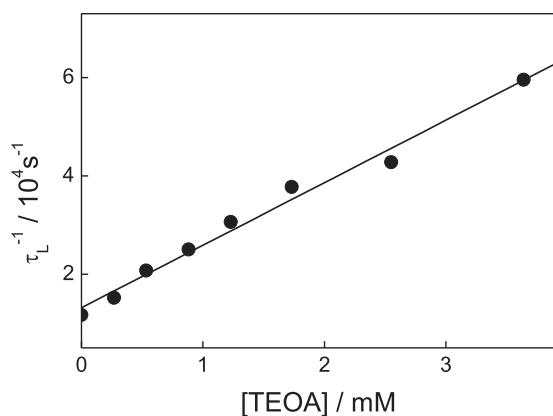
**Fig. 6.** Decay of thionine triplet ( $3 \times 10^{-5}$  M) in AOT at  $w = 10$  measured at 800 nm in the presence of TEOA 1.5 mM.



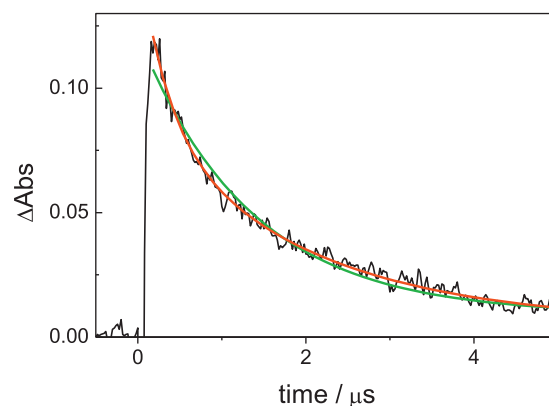
**Fig. 7.** Reciprocal of the short time component of the triplet decay vs. the mean occupation number of TEOA in AOT at  $w = 10$ .

surfactants concentrations employed the mean occupation number may be estimated as  $<0.1$ .

It was found that the absorption maximum is blue shifted, while the emission moves in the opposite direction, when  $w$  increases both in AOT and BHDC RMs. In Fig. 2 the absorption maximum wavelength and the Stokes shift are shown as a function of  $w$ . In both systems  $\lambda_{\max}$  and  $\Delta\nu$  move toward the values in water, represented by the dotted line in Fig. 2, although they are not reached even at the higher  $w$  investigated. It must be noted that in



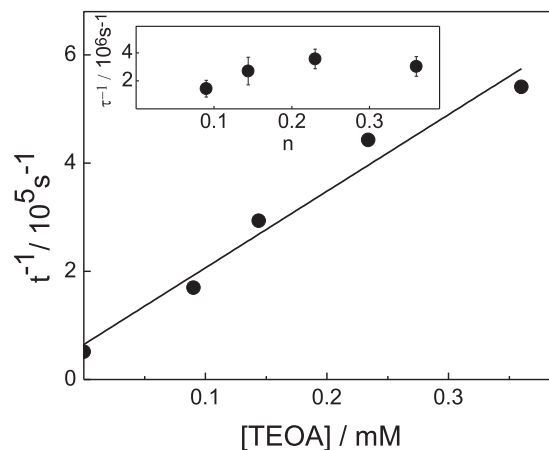
**Fig. 8.** Reciprocal of the long time component of the triplet decay vs. the analytical concentration of TEOA in AOT at  $w = 10$ .



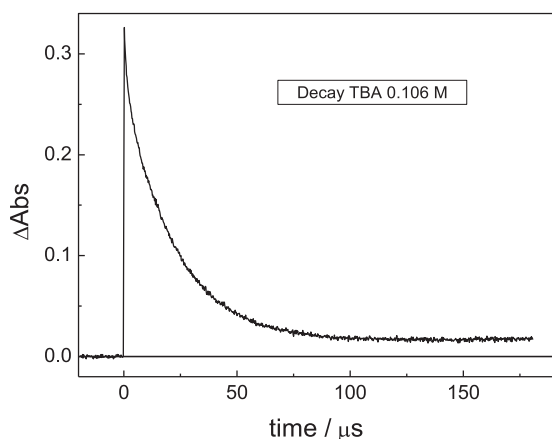
**Fig. 9.** Decay of thionine triplet ( $3 \times 10^{-5}$  M) in BHDC at  $w = 10$  measured at 800 nm in the presence of TEOA 0.36 mM. Green line: mono-exponential fit; red line: bi-exponential fit. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

BHDC/toluene the solutions become clouded at  $w > 10$  at room temperature.

It is generally assumed that the parameter  $w$  is directly proportional to micelle radius. At low  $w$  water molecules near or penetrating the interface experience very different environments compared with water molecules in water pools. The diverse behaviour of the dye may be explained in this way. When values of  $w = 10$  or higher are reached the interior of the RMs may be considered to be composed by bulk free water molecules. However, the medium sensed by the photophysical properties of  $\text{Th}^+$  points to a different situation. The maximum wavelength and Stokes shift, although showing a tendency towards the values in water, do not reach them even at the higher water content examined. This effect was observed for other dyes in reverse micellar systems [14,15,25]. This may be ascribed to the lower static polarity of the water pool compared to the bulk water [26]. In RMs the emission of the dye presents a red shift with respect to water. From this, it can be concluded that  $\text{Th}^+$  in both reverse micellar systems is localized in the interface. Although this is expected in AOT due to the positive charge dye and the negative interface, it is notable in the case of the positive interface of BHDC. In this case, it may be concluded that the dye resides in the interface co-micellizing with the surfactant.



**Fig. 10.** Reciprocal of the long time component of the triplet decay vs. the analytical concentration of TEOA in BHDC at  $w = 10$ . Inset: Reciprocal of the short time component of the triplet decay vs. the mean occupation number of TEOA in BHDC at  $w = 10$ .



**Fig. 11.** Triplet decay the  $\text{Th}^+$  ( $3 \times 10^{-5} \text{ M}$ ) measured at 800 nm in the presence of TBA 0.1 M in AOT at  $w = 10$ .

### 3.1. Triplet state

The triplet excited state of  $\text{Th}^+$  in BHDC and AOT RMs was investigated by laser flash photolysis upon excitation at 532 nm. The T-T absorption spectra taken immediately after the laser pulse in various media are shown in Fig. 3.

The spectrum in water presents a strong absorption at 770 nm and two lower intensity bands at 700 and 410 nm. This spectrum is red-shifted in solvents of lower polarity and in AOT and BHDC RMs. A summary of the absorption bands in different media is collected in Table 2. The spectrum in water and MeOH match with those reported in the literature [27,28]. Schlenker et al. [29] also reported a similar spectrum in RMs of cetyldimethylbenzylammonium-chloride, with maxima at 795, 720 and 425 nm.

At  $w = 2$  the spectrum in AOT is red shifted with respect to  $w = 10$  by ca. 10 nm in the far red region. On the other hand, in BHDC the spectrum is practically insensitive to the water content.

After the triplet decay in AOT a transient absorption remains with maxima at 780 and 400 nm may be ascribed to the protonated semireduced form of the dye [7], Fig. 4, while in BHDC the triplet lifetime is much longer and decays without any remaining absorption in the 800 nm region.

The spectral features are also coincident with those reported by Guha et al. for the pulse radiolysis generated semireduced form of the dye at pH 6 [30]. Semireduced thionine protonates at neutral pH ( $\text{pK}_a = 8.1$ ) and the protonated species presents bands at 400 and 770 nm [31]. The transient absorption after the triplet decay in BHDC shown in Fig. 5 is completely different from that in the AOT. This probably corresponds to the semi-oxidized and semireduced forms of the dye in a more basic media [30,32,33].

### 3.2. Triplet quenching by aliphatic amines

In order to assess the system dye-amine for ulterior interest of using it in photopolymerization studies in RMs, the quenching of the triplet  $\text{Th}^+$  by triethanolamine (TEOA) and tributylamine (TBA) in the reverse micelles was investigated.

### 3.3. Triplet quenching by TEOA in AOT

In the quenching by TEOA the triplet decay measured at 800 nm in AOT presents a non-exponential kinetics. A typical example is shown in Fig. 6.

The decay kinetics in Fig. 6 could be fitted by a bi-exponential function with lifetimes of 0.93 and 20.0  $\mu\text{s}$ . This biphasic decay might be the result of a fast intramicellar quenching and a slower

intermicellar process. A kinetic analysis for the triplet quenching in RMs by a quencher fully incorporated to the micelles leads to a non-exponential decay for the triplet and the kinetics may be described by [34],

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

where  $[T]_0$  is the initial triplet concentration immediately after the laser pulse,  $k_{qm}$  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. Eq. (1) is valid provided that

$$k_{qm} \gg k_{ex}[M] \quad (2)$$

If condition (2) is valid the fast initial decay is given by

$$[T] = [T]_0 \exp[-n(1 - \exp(-k_{qm}t))] \approx [T]_0 \exp(-nk_{qm}t) \quad (3)$$

From Eq. (3) the short time component of the bi-exponential fitting can be written as

$$(\tau_s)^{-1} = k_0 + k_{qm}n \quad (4)$$

A plot according to Eq. (4) of the reciprocal of the short lifetime can be seen in Fig. 7. From the slope a value of  $8.3 \times 10^5 \text{ s}^{-1}$  results for the unimolecular rate constant for the intramicellar triplet quenching by TEOA.

The slow process following the fast intramicellar quenching, may be ascribed to an intermicellar exchange process of the amine, and from Eq. (1) it can be expressed as

$$[T] = [T]_0 \exp[-(k_0 + k_{ex}[\text{TEOA}])t] \quad (5)$$

and the long lifetime of the bi-exponential fitting can be related to the amine concentration as

$$(\tau_L)^{-1} = k'_0 + k_{ex}[\text{TEOA}] \quad (6)$$

A fitting of the data to Eq. (6) can be seen in Fig. 8.

From the slope  $k_{ex} = 1.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  and since  $[\text{TEOA}] = 1.5 \text{ mM}$ , taken into account the value of  $k_{qm}$  given above, condition (2) is fulfilled, as required for the kinetic analysis. The value of the exchange rate constant is of the same order than the one found for the triplet quenching of the dye safranin-O in AOT RMs [19].

### 3.4. Triplet quenching by TEOA in BHDC

Thionine triplet is efficiently quenched by TEOA in cationic BHDC reverse micelles. Although the decay apparently can be fitted by a first order process, a closer examination show that it is not strictly mono-exponential and a bi-exponential decay clearly follows more closely the kinetics as can be seen in Fig. 9. The kinetics of quenching was treated with the same formalism as in the case of AOT. In BHDC the biphasic behaviour was very much less apparent and the determination of the fast intramicellar quenching was complicated by this fact. This was due to a fast photochemical process leading to the degradation of the dye that precludes the use of higher concentrations of TEOA. The results of the analysis of the decay are presented in Fig. 10.

From the plot in Fig. 10, an intermicellar quenching rate constant  $k_{ex} = 1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  results in BHDC while the rate constant estimated from the points shown in the inset for the intramicellar process is of the order of  $10^6 \text{ M}^{-1} \text{ s}^{-1}$ . The exchange rate constant is two orders of magnitude higher than in AOT and it reflects an intrinsic characteristic of BHDC reverse micelles since it is very similar to that determined by Jada et al. [21] by a totally different method. The intramicellar rate constant, although

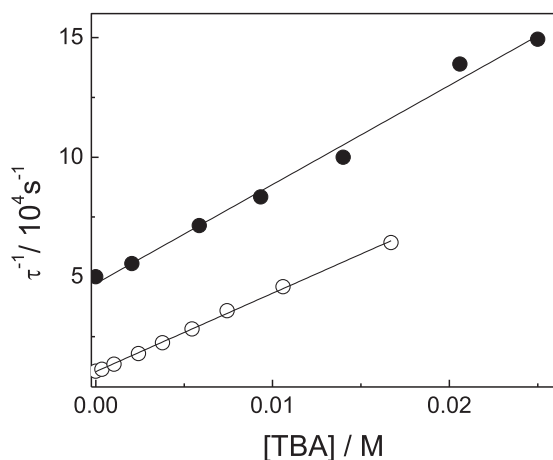


Fig. 12. Triplet quenching the  $\text{Th}^+$  ( $3 \times 10^{-5} \text{ M}$ ) by TBA in AOT at  $w = 10$  ( $\circ$ ) and in BHDC at  $w = 10$  ( $\bullet$ ).

affected by a considerable uncertainty is also higher than the corresponding value in AOT.

### 3.5. Quenching by TBA in AOT and BHDC

In the quenching by TBA the triplet decays appear as single exponential, Fig. 11. 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:

$$\tau^{-1} = k_o + k_q[\text{TBA}] \quad (7)$$

where  $\tau$  is the triplet lifetime,  $k_o$  is the first order rate constant for the triplet decay in the absence of the amine and  $[\text{TBA}]$  is the analytical concentration of the quencher. In Fig. 12 the plot of the first order decay rate constant of triplet  $\text{Th}^+$  vs. TBA concentration is shown.

From the slope of the linear fit a value of  $3.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  results for the apparent bimolecular quenching rate constant. Since TBA is a hydrophobic molecule appears extremely improbable that an appreciable fraction of thionine triplets is produced in micelles containing a TBA molecule. Thus any reaction between thionine triplets and TBA requires diffusion of the donor molecules from the bulk organic phase to the polar interior of the micelles where the cationic dye molecules must be located. The rate constant may be interpreted as the result of the two successive processes, diffusion and electron transfer quenching with TBA as electron donor. This explains the lower value as compared with TEOA.

A similar result was obtained in BHDC for the triplet quenching by TBA. The triplet decays appear as mono-exponential and a linear plot of the reciprocal lifetime as a function of the amine concentration can be seen in Fig. 12. From the slope an apparent rate constant of  $4.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  was obtained. It can be concluded that the quenching mechanism by an aliphatic amine located in the bulk organic phase is similar in AOT and BHDC.

In summary, the photophysics depends upon the localization of the dye molecules in the RMs. In spite of the dye being in its monocationic form, the dye localizes in the interface of the reverse micelles in both AOT and BHDC. 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. 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. It is efficiently quenched by an

aliphatic amine that can penetrate de inner core of the RMs, while it is protected to the quenching by a hydrophobic amine.

### Acknowledgments

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

### References

- [1] K. Kalyanasundaram, *Photochemistry in Microheterogeneous Systems*, Academic Press, London, 1987.
- [2] unlabelleda I. Capek, Fate of excited probes in micellar systems, *Adv. Colloid Interface Sci.* 97 (2002) 91–149; unlabelledb M. Andre's Durantini, R. Darío Falcone, J. Juana Silber, N. Mariano Correa, More evidence on the control of reverse micelles sizes. Combination of different techniques as a powerful tool to monitor AOT reversed micelles properties, *J. Phys. Chem. B* 117 (2013) 3818–3828.
- [3] B.K. Paul, S.P. Moulik, Uses and applications of microemulsions, *Curr. Sci.* 80 (2001) 990–1001.
- [4] A. Misra, K. Florence, M. Lalan, T. Shah, *Microemulsions in biotechnology and pharmacy: an overview*, in: Monser Fanun (Ed.), *Colloids in Biotechnology*, CRC Press, New York, 2011, pp. 381–416.
- [5] unlabelleda J.A. Gutierrez, M.A. Luna, N.M. Correa, J.J. Silber, R.D. Falcone, The impact of the polar core size and external organic media composition on micelle-micelle interactions: the effect on gold nanoparticle synthesis, *New J. Chem.* 39 (2015) 8887–8895; unlabelledb Abhijit Biswas, Alice Corani, Arunkumar Kathiravan, Yingyot Infahsaeng, Arkady Yartsev, Villy Sundstrom, Swati De, Control of the size and shape of TiO2 nanoparticles in restricted media, *Nanotechnology* 24 (2013) 195601.
- [6] V.E. Nicotra, M.F. Mora, R.A. Iglesias, A.M. Baruzzi, Spectroscopic characterization of thionine species in different media, *Dyes Pigm.* 76 (2008) 315–318.
- [7] S. Das, P.V. Kamat, Can H-aggregates serve as light-harvesting antennae? Triplet-Triplet energy transfer between excited aggregates and monomer thionine in aerosol-OT solutions, *J. Phys. Chem. B* 103 (1999) 209–215.
- [8] unlabelleda K.G. Mathaai, E. Rabinowitch, Studies of the thionine-ferrous iron reaction in a heterogeneous system, *J. Phys. Chem.* 66 (1962) 663–665; unlabelledb A.K. Jana, Solar cells based on dyes, *J. Photochem. Photobiol. A: Chem.* 132 (2000) 1–17.
- [9] unlabelleda J.P. Tardivo, A. Del Giglio, C.S. de Oliveira, D.S. Gabrielli, H.C. Junqueira, D.B. Tada, D. Severino, R. de F. Turchiello, M.S. Baptista, *Photodiagn. Photodyn. Ther.* 2 (2005) 175–191; unlabelledb X. He, X. Wu, K. Wang, B. Shi, L. Hai, Methylene blue-encapsulated phosphonate-terminated silica nanoparticles for simultaneous in vivo imaging and photodynamic therapy, *Biomaterials* 30 (2009) 5601–5609.
- [10] M.R. Rodrigues, F. Catalina, M.G. Neumann, Photoinitiation of MMA polymerization by thionine/amine systems in the presence of SDS micelles, *J. Photochem. Photobiol. A: Chem.* 124 (1999) 29–34.
- [11] P. Paul, M. Hossain, R.C. Yadav, G. Suresh Kumar, Biophysical studies on the base specificity and energetics of the DNA interaction of photoactive dye thionine: spectroscopy and calorimetric approach, *Biophys. Chem.* 148 (2010) 93–103.
- [12] S. Basu, D. Ray, B.B. Bhowmik, Photophysical studies of thionine dye in different solvents and PC liposome, *J. Chem.* 40 (2001) 460–465.
- [13] B.B. Bhowmik, M. Mukhopadhyay, Spectral and photophysical studies of thiazine dyes in Triton X-100, *Colloid Polym. Sci.* 266 (1988) 672–676.
- [14] D. Sahoo, S. Chakravorti, Spectra and dynamics of an ionic styryl dye in reverse micelles, *J. Photochem. Photobiol. A: Chem.* 205 (2009) 129–138.
- [15] 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.
- [16] G.V. Porcal, M.S. Altamirano, S.G. Bertolotti, C.M. Previtali, Organized media effect on the photochemical deoxygenation of resazurin in the presence of triethanolamine, *J. Photochem. Photobiol. A: Chem.* 219 (2011) 62–66.
- [17] unlabelleda G.V. Porcal, M.S. Altamirano, C.A. Glusko, S.G. Bertolotti, C.M. Previtali, Photophysical properties of the phenoxazin dyes resazurin and resorufin in soybean lecithin microemulsions, *Dyes Pigm.* 88 (2011) 240–246; unlabelledb G.V. Porcal, C.M. Previtali, S.G. Bertolotti, Photophysics of the phenoxazine dyes resazurin and resorufin in direct and reverse micelles, *Dyes Pigm.* 80 (2009) 206–211.
- [18] G.V. Porcal, E.M. Arbeloa, D.E. Orallo, S.G. Bertolotti, C.M. Previtali, Photophysics of safranin-O and phenosafranin in reverse micelles of BHDC, *J. Photochem. Photobiol. A: Chem.* 226 (2011) 51–56.
- [19] G.V. Porcal, C.A. Chesta, M.A. Biasutti, S.G. Bertolotti, C.M. Previtali, Quenching of the triplet state of safranin-O by aliphatic amines in AOT reverse micelles studied by transient absorption spectroscopy, *Photochem. Photobiol. Sci.* 11 (2012) 302–308.
- [20] J. Lang, A. Jada, A. Malliaris, Structure dynamics of water-in-011 droplets stabilized by sodium bis(2-ethylhexyl) sulfosuccinate, *J. Phys. Chem.* 92 (1988) 1946–1953.
- [21] 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) 381–395.
- [22] 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.
- [23] A. Rodríguez-Serrano, M.C. Daza, M. Doerr, C.M. Marian, A quantum chemical investigation of the electronic structure of thionine, *Photochem. Photobiol. Sci.* 11 (2012) 397–408 and references therein.
- [24] D.C. Crans, N.E. Levinger, The conundrum of pH in water nanodroplets: sensing pH in reverse micelle water pools, *Acc. Chem. Res.* 45 (2012) 1637–1645 and references therein.
- [25] S.M. Andrade, S.M.B. Costa, The aqueous environment in AOT and Triton X-100 (w/o) microemulsions probed by fluorescence, *Photochem. Photobiol. Sci.* 1 (2002) 500–506.
- [26] P. Hazra, N. Sarkar, Intramolecular charge transfer processes and solvation dynamics of coumarin 490 in reverse micelles, *Chem. Phys. Lett.* 342 (2001) 303–311.
- [27] J. Faure, R. Bonneauand, J. Jousot-Dubien, Étude en Spectroscopie par Eclair des colorants thiziniques en solution aqueuse, *Photochem. Photobiol.* 6 (1967) 331–339.
- [28] U. Steiner, M. Hafner, S. Sxhrene, H.E.A. Kramer, Increased quantum yield of photoreduction of dyes (A catalytic effect), *Photochem. Photobiol.* 19 (1974) 119–128.
- [29] W. Schlenker, T. Ulrich, U.E. Steiner, Magnetic field enhanced radical yield from triplet electron transfer reaction in reversed micelles, *Chem. Phys. Lett.* 103 (1983) 118–123.
- [30] S.N. Guha, P.N. Moorthy, K. Kishore, D.B. Naik, K.N. Rao, One-electron reduction of thionine studied by pulse radiolysis, *Proc. Indian Acad. Sci. (Chem. Sci.)* 99 (1987) 261–271.
- [31] J.M. Kelly, E.M. Tuite, W.J.M. Van der Putten, G.S. Beddard, G.D. Reid, Photophysical properties of thionine and methylene blue when bound to DNA, polynucleotides and nucleotides, in: V. Balzani, L. DeCola (Eds.), *Supramolecular Chemistry*, Kluwer, 1992, pp. 375–381.
- [32] D. Liu, P.V. Kamat, Dye-Capped semiconductor nanoclusters, one-electron reduction and oxidation of thionine and cresyl violet H-aggregates electrostatically bound to SnO<sub>2</sub> colloids, *Langmuir* 12 (1996) 2190–2195.
- [33] The existence of a semi-oxidized radical of thionine, absorbing at 520 nm has been indicated in experiments in pyridine by Maute (Thesis, University of Stuttgart, 1972) cited in Increase Quantum Yield of Photoreduction of dyes (A Catalytic Effect) Kramer et al. *Photochem. Photobiol.* 1974. Vol. 19, pp. 119–128.
- [34] unlabelled S.S. Atik, J.K. Thomas, Transport of photoproduct ions in water in oil microemulsions: movement of ions from one water pool to another, *J. Am. Chem. Soc.* 103 (1981) 3543–3550; unlabelled D.M. Togashi, S.M.B. Costa, Excited state quenching kinetics of zinc meso-tetrakis (N-methylpyridinium-4-yl) porphyrin by methyl viologen in AOT reverse micelles, *Phys. Chem. Chem. Phys.* 4 (2002) 1141–1150.