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# Deactivation of pyrene exciplexes in water-in-oil microemulsions prepared with benzylhexadecyldimethylammonium chloride

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## Abstract

The photophysical properties of exciplexes formed between pyrene and *N,N'*-dimethylaniline (DMA) or *p*-dicyanobenzene (DCB) were studied in benzene and benzylhexadecyldimethylammonium chloride–benzene–water microemulsions. The fluorescence of the exciplexes in benzene solution was strongly quenched by the addition of benzylhexadecyldimethylammonium chloride. Laser flash photolysis experiments were carried out in reversed micellar solutions. The transient absorption spectra showed the presence of the pyrene triplet state in all cases. For the pyrene–DMA system, the absorption of the pyrene radical anion was observed; however, the corresponding radical cation was not observed in the pyrene–DCB system. These results are discussed in terms of hydrophobic and electrostatic effects at the surfactant–water interface of the microemulsion.

*Keywords:* Benzylhexadecyldimethylammonium chloride; Deactivation; Exciplexes; Microemulsion; Pyrene

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## 1. Introduction

The properties of exciplexes have been studied extensively in homogeneous solutions. They are characterized by large dipole moments, and their fluorescence properties are strongly dependent on the polarity of the environment [1]. Exciplexes have also been studied in organized media, such as micelles [2], liposomes [3] and water-in-oil (W/O) microemulsions [4]. The excitation of pyrene (Py) in the presence of the electron donor *N,N'*-dimethylaniline (DMA) or the electron acceptor *p*-dicyanobenzene (DCB) leads to the emission of the corresponding exciplex in non-polar solvents [5]. In polar solvents, the emission of the exciplex is not observed, but radical ions from the electron transfer quenching of Py are produced with high efficiency [6,7].

Reversed micelles and W/O microemulsions are interesting systems for the study of the photophysical and photochemical properties of exciplexes. These organized systems consist of a homogeneous, thermodynamically stable solution of microdroplets of water surrounded by a surfactant monolayer and dispersed in an organic solvent [8]. In these systems, there are three different compartments in which small probe molecules can be solubilized: the internal water pool, the interface formed by the monolayer of surfactant molecules and the external organic phase. The behaviour of the Py–DMA exciplex in W/O microemulsions has received recent attention. It has been reported that the quenching of the exciplex by the water pools of the reversed micelles is very efficient and that the rate constants are comparable with those calculated by simple diffusion theory [9]. In laser flash photolysis experiments, only the triplet state of Py was observed on the microsecond timescale. A quenching model was proposed in which the exciplex formed in the organic phase penetrates the interface, where it is deactivated due to the higher polarity near the water pool region [10].

In Refs. [11,12], we reported the behaviour of exciplexes formed between Py derivatives and DMA in reversed micelles prepared with sodium bis(2-ethylhexyl)sulphosuccinate (AOT) or benzylhexadecyldimethylammonium chloride (BHDC). For AOT microemulsions, it was found that, when the Py group was linked by an alkyl chain to an ionic group, the fluorescence properties of the exciplexes were dependent on the length of the aliphatic chain [11]. For these systems, the emission maxima of the exciplexes shifted to the red and the fluorescence quantum yields decreased with increasing water content in the microemulsions. The transient absorption spectra showed only the characteristic absorption of the Py triplet state at 420 nm [12].

However, in solutions of BHDC reversed micelles, the behaviour of the exciplexes was quite different. The exciplex fluorescence was strongly quenched by the polar head of the

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BHDC molecules and the transient absorption spectra showed a maximum at 490 nm due to the radical anion of Py [12].

In this paper, we report a fluorescence and laser flash photolysis study of the properties of Py–DMA and Py–DCB exciplexes in BHDC–benzene–water microemulsions.

## 2. Experimental section

BHDC was obtained from Sigma. It was recrystallized several times from ethylacetate and dried under vacuum. Py, from Aldrich, was recrystallized from ethanol and dried under vacuum. DMA, from Merck, was distilled under vacuum immediately before use. DCB was purified by sublimation. Benzene, Sintorgan HPLC grade, was dried and distilled before use.

The fluorescence spectra of the exciplexes were measured with a Spex Fluoromax spectrofluorometer. Typically, $5 \times 10^{-6}$ M solutions of Py were used. The fluorescence quantum yields were measured relative to quinine bisulphate in 0.1 N sulphuric acid as standard. In all cases, DMA or DCB concentrations were large enough to reduce the fluorescence of Py to less than 5% of the original value. Under these conditions, the exciplex decay times could be obtained from the long tail of the decay curve by fitting it to a single exponential.

The fluorescence lifetime equipment used a nitrogen laser (ClOp, 0.1 mJ, 3 ns full width at half-maximum (FWHM)) as the excitation source. The sample was located in the cavity of a TRW 75A filter fluorometer. The signal of the photomultiplier was displayed, averaged and digitized by a Hewlett-Packard 54504A oscilloscope. It was then transferred via an IEEE interface to a PC, where it was processed. The signal-to-noise ratio allowed the decay curves to be analysed just over the range of two decades. The estimated error in the decay times was ±3% or ±0.5 ns, whichever was greater.

The apparatus for transient absorption experiments used a nitrogen laser (Laser Optics, 7 ns FWHM, 5 mJ per pulse) as the excitation source. The laser beam was directed at right angles to the analysing beam from a xenon arc lamp. The detection system comprised an f/4 monochromator and a red-extended photomultiplier (Hamamatsu R666 or RCA 4840). Transient signals were acquired in a similar manner to the fluorescence decays. The quantum yield determinations of the Py triplet state and Py radical anion were performed at 420 and 490 nm respectively. The extinction coefficient of the triplet–triplet absorption of the Py derivatives in benzene was taken as 20 900 $M^{-1}$ $cm^{-1}$ [13] and that of the Py radical anion as 49 200 $M^{-1}$ $cm^{-1}$ [14]. It was assumed that the extinction coefficients remain the same in the microemulsions. The triplet absorption at 470 nm of a solution of zinc tetraphenylporphyrin in benzene was used as a standard for the quantum yield determinations [15]. The concentration of Py was around $5 \times 10^{-5}$ M and matched the absorbance of the standard solution at the laser excitation wavelength.

All experiments were performed under a controlled temperature of 30 °C. This temperature is necessary to avoid problems related to the coalescence of microdroplets in the BHDC solution. The solutions were deoxygenated by nitrogen bubbling. Care was taken to prevent solvent and/or water evaporation.

## 3. Results and discussion

### 3.1. Experiments without the addition of water

The addition of DMA or DCB to benzene solutions of Py results in the quenching of Py fluorescence. The fluorescence quenching rate constants of Py by both quenchers are similar ($4 \times 10^9$ $M^{-1}$ $s^{-1}$). The quenching processes are accompanied by the characteristic emission of Py–DMA and Py–DCB exciplexes. The absorption spectrum of the fluorescent probe does not change in the presence of either quencher. Moreover, the fluorescence excitation spectra observed at the monomer and exciplex emission maxima are coincident, thus confirming the lack of ground state association between Py and the quencher molecules.

The addition of BHDC to Py–DMA or Py–DCB benzene solutions quenches the fluorescence of both exciplexes. In Fig. 1, this effect is shown for the Py–DMA exciplex. No changes are observed in the absorption or fluorescence spectra of Py in the presence of BHDC. These results confirm that the fluorescence quenching is due to exciplex–surfactant interactions. In Table 1, the quantum yields ($\Phi_f$) of exciplex

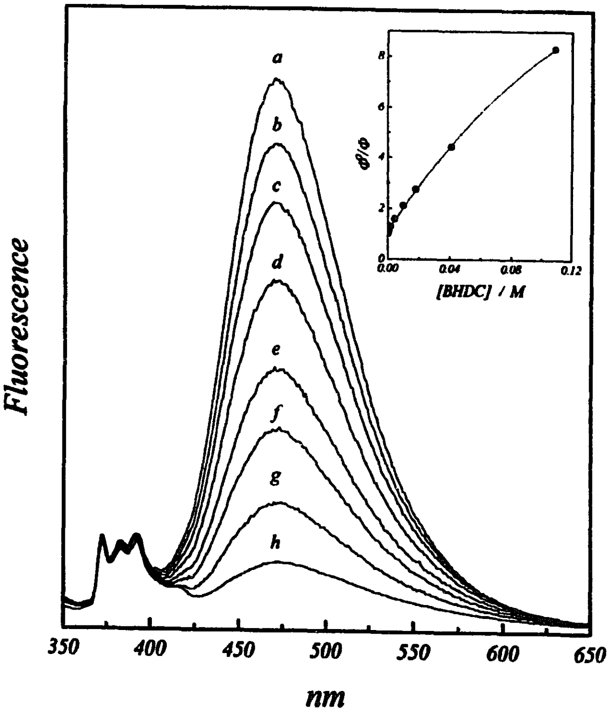


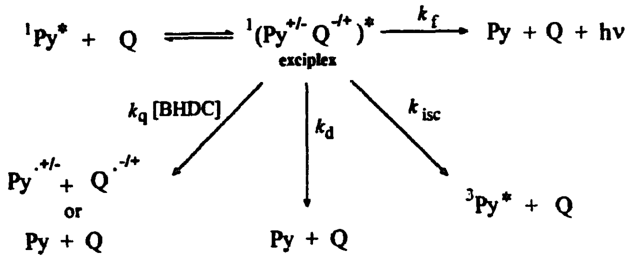
Fig. 1. Fluorescence spectra of Py–DMA exciplex in benzene solutions at different BHDC concentrations: (a) 0 mM; (b) 0.5 mM; (c) 1.6 mM; (d) 4.2 mM; (e) 9.9 mM; (f) 18.0 mM; (g) 41.0 mM; (h) 109 mM.

Table 1
Fluorescence parameters of the Py–DCB and Py–DMA exciplexes in BHDC–benzene–water microemulsions at 30 °C

| Py–DCB | | | Py–DMA | | |
|---|---|---|---|---|---|
| [BHDC] (mM) | $\Phi_f$ | $\tau_f$ (ns) | [BHDC] (mM) | $\Phi_f$ | $\tau_f$ (ns) |
| 0 | 0.175 | 72 | 0 | 0.234 | 101 |
| 1.5 | 0.137 | 53 | 1.6 | 0.182 | 90 |
| 6.4 | 0.102 | 39 | 4.2 | 0.149 | 73 |
| 16 | 0.079 | 28 | 9.9 | 0.110 | 58 |
| 50 | 0.046 | 18 | 41 | 0.054 | 29 |
| 85 | 0.035 | 13 | 109 | 0.029 | 20 |
| *R* ([BHDC] = 85 mM) | $\Phi_f$ | $\tau_f$ (ns) | *R* ([BHDC] = 109 mM) | $\Phi_f$ | $\tau_f$ (ns) |
| 0 | 0.035 | 13 | 0 | 0.029 | 20 |
| 5 | 0.053 | 26 | 5 | 0.049 | 31 |
| 10 | 0.068 | 36 | 10 | 0.069 | 46 |
| 20 | 0.083 | 43 | 20 | 0.094 | 56 |

emission at several BHDC concentrations are presented. The fluorescence emission maxima of the exciplexes are independent of the BHDC concentration. They are located at the same wavelengths as in benzene, i.e. 435 nm and 471 nm for the Py–DCB and Py–DMA systems respectively.

The fluorescence quenching of exciplexes by quaternary ammonium salts in low polarity solvents is well established [16–19]. In aprotic solvents of low dielectric constant, bulky quaternary ammonium salts exist mainly as ion pairs [20]. These ion pairs are believed to be the quenching species and, in some cases, a fluorescent intermediate complex between the exciplex and the salt can be observed [21]. The above model can be used to explain the quenching of both exciplexes by BHDC shown in Fig. 1 and Table 1. Therefore the quenching of the Py–DMA and Py–DCB exciplexes by BHDC can be represented by the scheme shown below, where Q represents DMA or DCB.



The emission maxima of the exciplexes in BHDC solution are at the same wavelengths as in benzene; this indicates that the exciplexes are formed in the organic phase. The Stern–Volmer plots obtained from the fluorescence quantum yields or fluorescence decay times of the exciplexes show a downward curvature with increasing surfactant concentration (inset in Fig. 1). This deviation can be explained by a further aggregation of the BHDC ion pairs which reduces the effective quencher concentration. From the initial slope of the Stern–Volmer plots, we obtained a quenching rate constant by BHDC of (1–2) × $10^9\ \mathrm{M^{-1}\ s^{-1}}$ for both exciplexes. This value is of the same order of magnitude as those reported previously in the literature [16,17,19,21].

Laser flash photolysis experiments were performed to obtain more information on the fate of the exciplexes. In pure benzene solutions, the transient spectra of Py–DMA and Py–DCB systems at 1.5 μs after the laser pulse show absorption in the regions 400–420 nm and 520 nm due to the Py triplet state. These transient absorption spectra were obtained at a sufficiently high DMA or DCB concentration to yield a quenching fraction of the Py singlet state larger than 95%. Under these experimental conditions, all the triplet–triplet absorption observed must be due to the decay of the exciplex to the triplet state. However, in BHDC solutions, the transient species observed at 1.5 μs after the laser pulse for the Py–DMA system are the triplet state of Py, the Py radical anion at 495 nm and the DMA radical cation in the region 440–470 nm. In Table 2, the quantum yields of the Py radical anion and the Py triplet state for the Py–DMA system in BHDC–benzene solutions are given at several surfactant concentrations. It can be seen that the principal transient observed is the triplet state of Py and its quantum yield decreases with increasing BHDC concentration. The quantum yield of the radical anion is small and remains almost unchanged with increasing BHDC concentration.

The transient absorption spectrum of the Py–DCB system in BHDC solution without added water shows absorption due principally to the triplet state of Py (Fig. 2). Under our experimental conditions, we detected only a very weak absorption around 460 nm, ascribed to the radical cation of Py. In pure benzene, the triplet quantum yield of Py is large ($\Phi_T = 0.76$) and decreases as the BHDC concentration increases.

The presence of radical ions in a non-polar solvent containing surfactant molecules can be explained by the interchange of counterions between the exciplex and the surfactant molecules [18]

$$^1(\mathrm{Py}^{\cdot-}\mathrm{DMA}^{\cdot+})^* + \mathrm{BHD^+Cl^-} \rightarrow \mathrm{Py}^{\cdot-}\mathrm{BHD}^+ + \mathrm{DMA}^{\cdot+}\mathrm{Cl}^-$$

or

Table 2
Pyrene radical ion and pyrene triplet quantum yields for the Py–DCB and Py–DMA systems in BHDC–benzene–water microemulsions at 30 °C

| [BHDC] (mM) | Py-DMA | | | | | |
|---|---|---|---|---|---|---|
| | $R=0$ | | $R=10$ | | $R=20$ | |
| | $\Phi_{\text{ion}}$ | $\Phi_T$ | $\Phi_{\text{ion}}$ | $\Phi_T$ | $\Phi_{\text{ion}}$ | $\Phi_T$ |
| 0 | – | 0.483 | – | – | – | – |
| 50 | 0.062 | 0.315 | 0.071 | 0.359 | 0.101 | 0.371 |
| 109 | 0.062 | 0.277 | 0.130 | 0.303 | 0.190 | 0.296 |
| 146 | 0.070 | 0.259 | 0.145 | 0.283 | 0.229 | 0.263 |
| 205 | 0.066 | 0.258 | 0.194 | 0.259 | 0.280 | 0.230 |

| [BHDC] (mM) | Py-DCB | | | | | |
|---|---|---|---|---|---|---|
| | $R=0$ | | $R=10$ | | $R=20$ | |
| | $\Phi_{\text{ion}}$ | $\Phi_T$ | $\Phi_{\text{ion}}$ | $\Phi_T$ | $\Phi_{\text{ion}}$ | $\Phi_T$ |
| 0 | – | 0.755 | – | – | – | – |
| 50 | <0.01 | 0.191 | – | 0.440 | – | 0.539 |
| 100 | | 0.195 | – | 0.319 | – | 0.434 |
| 140 | <0.01 | 0.185 | – | 0.277 | – | 0.373 |
| 200 | | 0.173 | – | 0.256 | – | 0.305 |

–, Not observed.

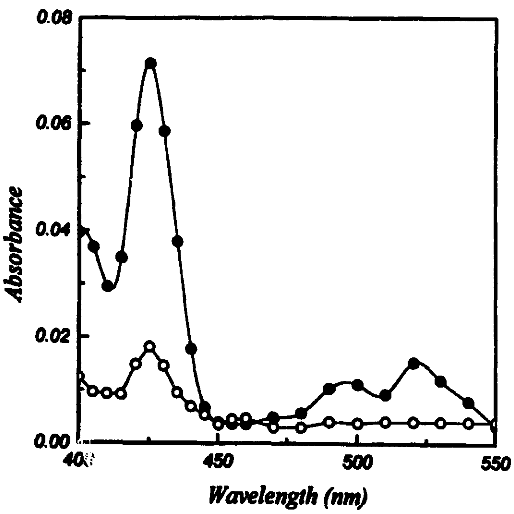


Fig. 2. Transient absorption spectra of Py–DCB system in pure benzene (●) and in BHDC (100 mM)–benzene ($R=0$) (○).

$$^1(\mathrm{Py}^{\cdot+}\mathrm{DCB}^{\cdot-})^* + \mathrm{BHD}^+\mathrm{Cl}^- \rightarrow \mathrm{Py}^{\cdot+}\mathrm{Cl}^- + \mathrm{DCB}^{\cdot-}\mathrm{BHD}^+$$

The triplet quantum yields of the Py–DMA and Py–DCB systems in pure benzene are reduced by the addition of small portions of BHDC. This result agrees with the exciplex quenching model by surfactant molecules proposed above.

### 3.2. Experiments with the addition of water

When water is added to a given BHDC–benzene solution, W/O microemulsions are formed. In these conditions, the fluorescence of the exciplexes increases progressively with increasing $R=[\text{water}]/[\text{BHDC}]$. This may be explained by the association of water molecules with the surfactant ionic heads. In this way, the surfactant ionic pairs are destroyed, and exciplex quenching due to these ionic pairs diminishes. Therefore the fluorescence of the exciplexes starts to recover. However, for a given constant $R$ (20 or higher), there is still a BHDC concentration quenching effect. This quenching can be explained by the model proposed by Kikuchi and Thomas [9]. In this case, quenching occurs when the exciplex in the organic phase is intercepted by a single reversed micelle and is able to penetrate the internal water pool. In this region, the high polarity of the medium suppresses the exciplex emission. This exciplex quenching mechanism by water pools becomes operative at $R$ values at which water pools, and therefore "true" reversed micelles, are formed. In BHDC–benzene solutions, this occurs for $R>8$ [22].

Taking into account the formation of reversed micelles, the exciplex quenching by water pools can be represented by a scheme similar to that given in Section 3.1, where $k_q[\text{BHDC}]$ is changed to $k_{qm}[\text{Mic}]$. The bimolecular quenching rate constant by water pools ($k_{qm}$) can be obtained using the decay times of the exciplexes in pure benzene ($\tau_0$) and the decay times in the presence of reversed micelles ($\tau$) according to the equation

$$\frac{1}{\tau}=\frac{1}{\tau_0}+k_{qm}[\text{Mic}] \qquad (1)$$

where [Mic] can be obtained by dividing the BHDC concentration by the aggregation number of the reversed micelles, taken as 185 and 420 for BHDC in benzene at $R=10$ and $R=20$ respectively [9]. Table 3 shows the $k_{qm}$ values for the quenching of Py–DMA and Py–DCB exciplexes by BHDC reversed micelles in benzene at $R=10$ and 20. The rate con-

Table 3
Quenching rate constants for the Py–DMA and Py–DCB exciplexes by BHDC reversed micelles in benzene at 30 °C

| R | $k_{qm}$ ($\times 10^{-10}$ M$^{-1}$ s$^{-1}$) | | |
|---|---|---|---|
| | Eq. (1) | Eq. (2) | Eq. (3) |
| 10 | 2.0 (1.8) [a] | 1.0 [a] | 1.0 [a] |
| 20 | 3.0 (3.1) [a] | 2.4 [a] | 1.1 [a] |
| 10 | 3.0 [b] | 2.9 [b] | – [b] |
| 20 | 4.5 [b] | 4.1 [b] | – [b] |

[a] Py–DMA.
[b] Py–DCB. Values in parentheses from Ref. [9].

stants are large and increase with the size of the water pools; the values are comparable with the diffusion-controlled rate constants calculated by classical diffusion theory, and agree with those reported in the literature for the Py–DMA [9] and methylpyrene–DMA [12] systems.

Laser flash photolysis experiments on the Py–DMA system indicate that, when reversed micelles at $R=10$ and 20 are present in the solution, the Py radical anion quantum yield increases with increasing surfactant concentration (Table 2). The above effect on the transient absorption spectra of the Py–DMA system in BHDC–benzene–water ($R=10$) is shown in Fig. 3. As the surfactant concentration is increased, an important increase in the radical anion absorption at 495 nm can be observed. At the same time, the triplet yield, associated with the band at 420 nm, decreases. Furthermore, the radical ion quantum yield is dependent on $R$, and increases with increasing $R$ at all surfactant concentrations. The Py triplet quantum yields are slightly dependent on the amount of water in the microemulsion (Table 2).

For the Py–DCB system, laser flash photolysis experiments show that, in solutions with $R \geq 10$, the Py radical cation absorption is not observed. However, the quantum yield of the Py triplet state clearly increases with the addition of water (Table 2).

In the presence of "true" reversed micelles ($R \geq 10$), the transient behaviour agrees with the exciplex quenching model by water pools. From this model, the following equations can be obtained for the dependence of the triplet and radical ion quantum yields on the concentration of BHDC

$$\frac{\Phi_T^0}{\Phi_T} = 1 + K_{SV}[\mathrm{Mic}] = 1 + \frac{K_{SV}}{N_{agg}}[\mathrm{BHDC}] \qquad (2)$$

and

$$\frac{1}{\Phi_{ion}} = \frac{1}{f_Q}\left(1 + \frac{1}{K_{SV}[\mathrm{Mic}]}\right) = \frac{1}{f_Q}\left(1 + \frac{N_{agg}}{K_{SV}[\mathrm{BHDC}]}\right) \qquad (3)$$

where $N_{agg}$ is the micellar aggregation number for each $R$ value, $f_Q$ is the product of the quenching probability of an excited Py molecule by the probability that the initially formed ion pair leads to charge separation and $K_{SV}$ ($k_{qm}\tau_{exc}^0$) is the Stern–Volmer constant. In Fig. 4, the Stern–Volmer plots are shown for the quenching of the triplet state by BHDC for the Py–DCB and Py–DMA systems at $R=20$. The double inverse plots according to Eq. (3) for the quantum yield of the radical ions of the Py–DMA system at $R=10$ and $R=20$ are shown in Fig. 5. In both cases, linear plots can be observed, and from their intercepts and slopes we can calculate the bimolecular quenching rate constants ($k_{qm}$) of the exciplexes by the water pools. These results are given in Table 3. The rate constants obtained from triplet quenching and radical ion yields are smaller than those obtained by fluorescence quenching for both exciplexes. However, considering the differences in the experimental measurements and the treatment of the results, the correspondence between the three sets of results is acceptable.

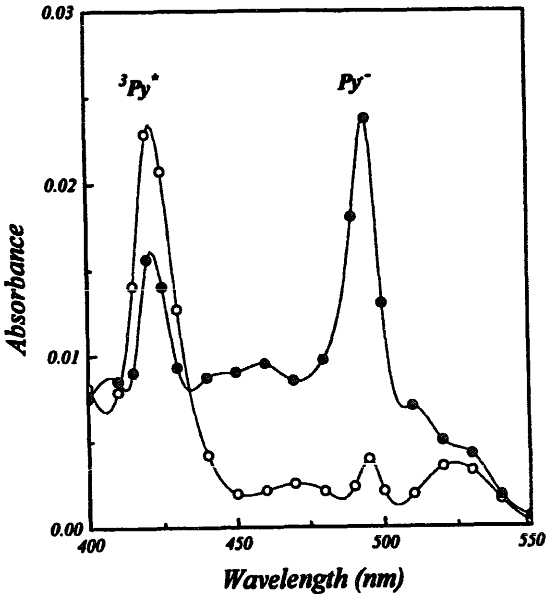


Fig. 3. Transient absorption spectra of Py–DMA system in BHDC–benzene–water at $R=20$: ○, [BHDC] = 26 mM; ●, [BHDC] = 205 mM.

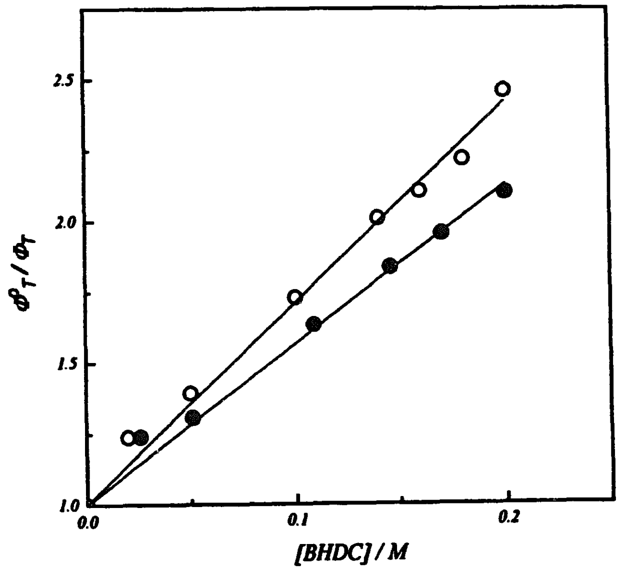


Fig. 4. Stern–Volmer plots of the pyrene triplet quantum yields in BHDC–benzene–water ($R=20$) microemulsions: ○, Py–DCB system; ●, Py–DMA system.

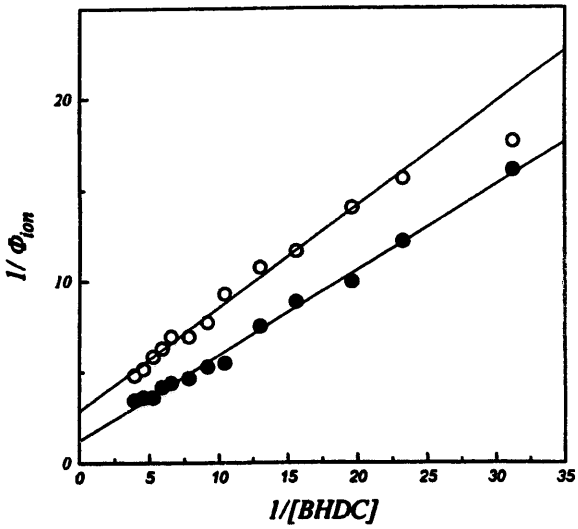


Fig. 5. Double inverse plot of the radical ion quantum yields vs. the BHDC concentration for the Py–DMA system in BHDC–benzene–water microemulsions at different $R$ values: ○, $R=10$; ●, $R=20$.

The lack of free radical ions in the Py–DCB system, when water is present in the solution, may be due to a fast back electron transfer reaction of the radical ions induced by the micellar interface. This recombination reaction seems to be controlled by hydrophobic and electrostatic effects. The Py radical cation is a bulky organic ion with a large hydrophobicity. Therefore the electrical repulsion of the positive interface of BHDC is not large enough to expel the radical cation from the interface to the water pool. Most probably, the Py radical cation will remain associated with the interface, forming part of the micelle together with the BHDC molecules. The smaller DCB radical anion is also retained at the cationic micellar interface by electrostatic interactions. Thus both ions will be in close proximity and will suffer a fast recombination reaction in the submicrosecond time window. The increase in the triplet quantum yields for the Py–DCB system as $R$ increases can be explained by the model used to explain the increase in the fluorescence quantum yields.

For the Py–DMA system, the micellar interface will favour charge separation. The bulky Py radical anion will be localized at the micellar interface by electrostatic and hydrophobic interactions and the smaller DMA radical cation will be expelled towards the water pool. In this way, the cationic interface behaves as a barrier for the recombination of radical ions. This interpretation can be extended to previous results in anionic reversed micelles prepared with AOT [12], where the Py radical anion could not be observed in the transient absorption spectrum of the 1-methylpyrene–DMA system. Similar interface effects on charge separation have been observed in normal micelles for Py–DMA [23,24] and Py–indole [25] systems.

The increase in the radical ion quantum yield with increasing $R$ and surfactant concentration, shown in Table 2, can be explained by the fast exchange of material between reversed micelles which occurs in BHDC–benzene–water microemulsions [26]. In this system, the intermicellar exchange rate constant ($k_c$) increases with $R$. Furthermore, the probability of material exchange is proportional to the concentration of reversed micelles. Therefore the efficiency of charge separation increases with increasing reversed micelle concentration and increasing size of the water pools.

In conclusion, the quantum yield of photoproduction of radical ions is strongly dependent on the molecular donor–acceptor precursor pair. The charge and hydrophobicity of the geminate ions, together with the charge of the micellar interface, are important factors during the course of a photochemical reaction occurring in solutions of reversed micelles.

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