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Influence of Polarity and Viscosity of the Micellar Interface on the Fluorescence Quenching of Pyrenic Compounds by Indole Derivatives in AOT Reverse Micelles Solutions

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The fluorescence quenching of the pyrene derivatives (4-(1-pyrenyl)butyl) trimethylammonium bromide (PBTMA), (1-(1-pyrenyl)methyl) trimethylammonium iodide (PMTMA), and 1-pyrene sulfonic acid (PSA) by indole methyl substituted in positions 1 and 2, tryptophan and tryptamine, was studied in AOT/heptane reverse micelles as a function of R = [water]/[AOT]. In these systems the pyrenic probes are associated to the micellar interface. Bulk and intramicellar quenching rate constants were determined for neutral indoles. The quenching rate constants of PBTMA by indole or 1,2-dimethylindole increase with R, whereas for those for PMTMA or PSA by indole the increment is much smaller. For the quenchers, tryptophan and tryptamine, that are bound to the interface of the reverse micelle, the bimolecular intramicellar quenching rate constant is much lower than in water. The results can be explained by a high microviscosity of the interface, and a micropolarity similar to that sensed by other probes. Moreover, the observed trend in the rate constants when R is varied is in line with the reported changes in micropolarity and microviscosity. Laser flash photolysis experiments show that in these systems the main result of the quenching process is the formation of the excited triplet of the probe.

Key Words: **reverse micelles; AOT; fluorescence quenching; indolic compounds; laser photolysis; microviscosity; micropolarity.**

INTRODUCTION

The study of photophysical and photochemical processes in reverse micelles has received considerable attention during the last years (1, 2). These aggregates are present in solutions of various amphiphiles in nonpolar organic solvents. Their structure is such that the polar headgroups of the amphiphile constitute the core of the aggregate, and the hydrophobic tails extend into the surrounding solution. They are able to solubilize fairly large amounts of water in the inner polar core. In these systems there are three compartments in which small probe molecules can be solubilized, the internal water pool, the interface formed by a monolayer of the surfactants' molecules, and the external organic phase (1, 3, 4). The existence of nanometer-sized water droplets in these aggregates makes these structures an appropriate model for characterizing the critical features of aqueous microphases in hydrophobic environments such as those found within living cells.

One of the excited state processes that was the subject of a large number of papers is the fluorescence quenching of probes bound to the micellar interface. It was investigated for quenchers dissolved in the organic phase (5–12) the water pool (13–16), and for quenchers partitioned between the water pool and the interface, or between the interface and the organic phase (8, 11). In order to interpret the results of the quenching processes in reverse micelles, a detailed knowledge of the mechanism in homogeneous solutions is necessary.

The interaction between indolic compounds and excited molecules has received great attention in the last decades, due to the relevant role that the indolic moiety of tryptophan could play in photobiological processes. In particular the quenching of the excited singlet state of pyrene by indole derivatives in homogeneous solvents and normal micelles has been studied extensively during recent years (17–20). The rate constant depends on the solvent polarity (17); it increases with an increase in the dielectric constant of the solvent and it is near diffusion controlled in water (18). In nonpolar solvents, indole derivatives have been shown to form emissive exciplexes with pyrene and 1-cyanopyrene (20). In polar solvents and micellar solutions the exciplex emission is not observed, and the electron transfer nature of the quenching process was confirmed by the transient absorption spectra of the long-lived species remaining after the quenching event (21, 22). Furthermore, the photobleaching of pyrene was observed in the presence of indole, together with the transient formation of the hydropyrenyl radical and the pyrene radical cation (22). The reaction was not observed with 1-methylindole. The reaction quantum yield is highly dependent upon the solvent polarity, and a mechanism that involves a proton transfer following the initial electron transfer was proposed (22).

In normal micelles the quenching of pyrene has been employed to determine the partition coefficient of indole and tryptophan (18, 19). The effect of the charged micellar inter-

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face on the quantum yield of the photobleaching process has also been reported (22). However, we are not aware of studies of the quenching reaction of pyrene by indolic compounds in reverse micelles solutions. It is well known that the polarity and viscosity of the water core and the interface are functions of the micellar size, which in turn is proportional to the molar ratio of water to surfactant (13, 23, 24). In a previous work (25) we have shown, from the fluorescence behavior of exciplexes formed between cationic pyrene derivatives and N,N′-dimethylaniline (DMA) in AOT reverse micelles, that the interface polarity depends on the location of the pyrenyl moiety and the amount of water dissolved into the solution. Thus, taking advantage of the features of the electron transfer quenching reaction of pyrene derivatives by indoles and the tunable properties of the water pool and micellar interface of the reverse micelles, we undertook the present study.

Here we present results on the fluorescence quenching by indolic compounds of probes anchored to the AOT (Sodium bis(2-ethylhexyl)sulfosuccinate) reverse micelles' interface or comicellizing with the surfactant. The effect of the water content, measured as R = [water]/[AOT], on the quenching rate constants was investigated. The quenchers include compounds that reside mainly in the organic phase, N-methyl indoles, molecules that are partitioned between the organic phase and the interface, indole itself, and the biological relevant indole derivatives, tryptophan and tryptamine, that are located in the interface (5, 7, 11). The probes are the pyrene derivatives 1-pyrenesulfonic acid (PSA), 1-pyrenemethyltrimethylammonium iodide (PMTMA) and 1-pyrenebutyltrimethylammonium bromide (PBTMA). In AOT reverse micelles these molecules are known to be associated to the interface (8, 11, 26). The experimental results indicate that the intramicellar quenching rate constants increase with R, but they are much lower than in homogeneous solvents. Transient absorption spectra obtained by laser flash photolysis of some pyrene derivatives in the presence of indole are also reported. The results are analyzed considering the polarity and viscosity of the interface.

EXPERIMENTAL

The AOT was bought from Sigma. It was dried under vacuum and used without further purification. PBTMA, PMTMA, and PSA, were products from Molecular Probes and employed as received. The indole, 1-methylindole (1-MI), 1,2-dimethylindole (1,2-DMI), tryptamine, and tryptophan were from Sigma. They were purified by recrystallization or vacuum distillation. The water was triply distilled.

All experiments were done under controlled temperature at 25 ± 1°C. All solutions were deoxygenated by nitrogen bubbling. Care was taken to avoid solvent and/or water evaporation. Typically, 5×10^{-6} M solutions of the probes were employed for fluorescence studies. Under these experimental conditions the average number of probes per micelle is much less than one. In some cases the water pool was prepared with HCl solutions adjusted to pH 3 to assure that tryptamine was in its cationic form and therefore anchored to the interface. The AOT concentration was 0.1 M and R (= $[H_2O]/[AOT]$) was varied between 0 and 30.

Fluorescence spectra were obtained with a Spex Fluoromax spectrofluorometer. The fluorescence lifetime equipment consisted of a nitrogen laser (CIOp, 0.1 mJ, and 3 ns 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 computer, where it was processed. The signal-to-noise ratio was compatible with the analysis of the decay curves just over a two-decade range. The estimated error in the decay times was ±3% or ± 0.5 ns, whichever was greater. Transient absorption spectra were measured with a Spectron SL400 Nd-YAG system generating 355 nm laser pulses (~8 ns pulse width). The laser beam was defocused in order to cover all of the path length (10 mm) of the analyzing beam from a 150 W Xe lamp. The experiments were performed with rectangular quartz cells with right-angle geometry. The detection system comprised a PTI monochromator coupled to a Hamamatsu R666 PM tube. The signal acquisition and processing were similar to the fluorescence lifetime measurements.

RESULTS

I. Quenching by Indole, 1-Methylindole, and 1,2-Dimethylindole

The fluorescence emission spectra and decay times of PBTMA, PSA, and PMTMA in 0.1 M AOT/heptane/water reverse micelles solutions were similar to those previously reported (26, 25). The addition of the indole derivatives quenches the fluorescence of the pyrenic probes without causing changes in their absorption spectra. Within the lifetime resolution of our experimental setup, the decay of the pyrene derivatives in the reverse micelles in the absence and in the presence of the indoles appears as monoexponential in all cases. The shape of the emission spectra was not altered by the quenching process and photobleaching of the probes was not observed in our experimental conditions.

In a previous work on the fluorescence behavior of indole derivatives in AOT (11), we showed that the fluorescence emission spectra of 1,2-DMI in AOT/heptane solutions, at different AOT concentrations and several R values, are similar to those observed in n-heptane. From these results it was concluded that 1,2-DMI is located mainly in the *n*-heptane phase. On the other hand, the fluorescence spectrum of indole was dependent on the AOT concentration, indicating that this quencher is partitioned between the organic phase and the micellar aggregates.

TABLE 1
Bulk Quenching Rate Constants in AOT 0.1 *M*/Heptane Reverse Micelles at 25°C at $R = 30$

	$k_q/10^9\ M^{-1}\ s^{-1}$					
	PBTMA		PMTMA		PSA	
Quencher	AOT	EtOH	AOT	EtOH	AOT	EtOH
1-methylindole	0.008	0.049	1.1	3.2	1.1	2.9
1,2-dimethylindole	0.30	1.7			1.1	2.6

For the quenchers localized in the organic phase, 1-MI and 1,2-DMI, the quenching rate constant can be expressed in terms of the bulk indole concentration. The bimolecular quenching rate constants k_q, were calculated by

$$\frac{1}{\tau} = \frac{1}{\tau_o} + k_q[In], \qquad [1]$$

where τ and τ_o are the fluorescence decay times in the presence and the absence of the indole derivative, respectively, and [*In*] is the total analytical concentration of the indolic compound in the micellar system. In all the cases linear plots of $1/\tau$ vs [*In*] were obtained. For some systems the quenching rate constants were also determined by measuring fluorescence intensities. Good agreement was obtained with the lifetime data. Rate constants obtained by means of Eq. [1] are called bulk rate constants, and they are collected in Table 1. For the sake of comparison the rate constants in ethanol, determined in the same way, are also included. Figure 1 shows the dependency of k_q with *R* for the quenching of PBTMA by 1,2-DMI.

Since indole is partitioned between the organic phase and the micellar interface, the quenching rate constants are better expressed in terms of the indole concentration in the micellar phase. Equation [1] is now written in the modified form given by Eq. [2].

$$\frac{1}{\tau} = \frac{1}{\tau_o} + (k_q)_{mic}[In]_{mic}, \qquad [2]$$

where $(k_q)_{mic}$ is the bimolecular rate constants in the micellar pseudophase (8), and $[In]_{mic}$ is the indole concentration in the micelle, which can be evaluated from the indole partition constant defined as

$$K = \frac{[In]_{mic}}{[In]_{hep}[AOT]} = \frac{\bar{n}}{[In]_{hep}N_{agg}}. \qquad [3]$$

The volume of the interfacial region is assumed to be the volume occupied by the monolayer of the AOT molecules. The partition constant of indole in AOT reverse micelles was found to be $34 \pm 4\ M^{-1}$ and independent of *R* (11). In Eq. [3] $\bar{n} = [Q]/[M]$ is the mean number of quencher molecules (Q) per reverse micelle (M) and N_{agg} is the aggregation number of AOT at a given *R*. The aggregation numbers and the volume occupied by one AOT molecule (636 cubic Armstrong) reported by Lang *et al.* (16) were used. The values of $(k_q)_{mic}$ for indole as quencher at $R = 30$ and at occupation numbers larger than 1 are reported in Table 2. The effect of the water content is shown in Fig. 1.

In all cases, it is observed that k_q or $(k_q)_{mic}$ are smaller in the reverse micelle solution than in ethanol and that they increase with *R*. However, the variation of the quenching rate constant with *R* is dependent on the pyrene derivative. For indole as quencher, the increment for PBTMA is larger than for PMTMA or PSA. At the same *R* value the $(k_q)_{mic}$ values follow the order PSA $\cong$ PMTMA $\gg$ PBTMA. On the other hand, for PBTMA with indole or 1,2-DMI as quenchers the rate constants reach a plateau at $R \geq 20$.

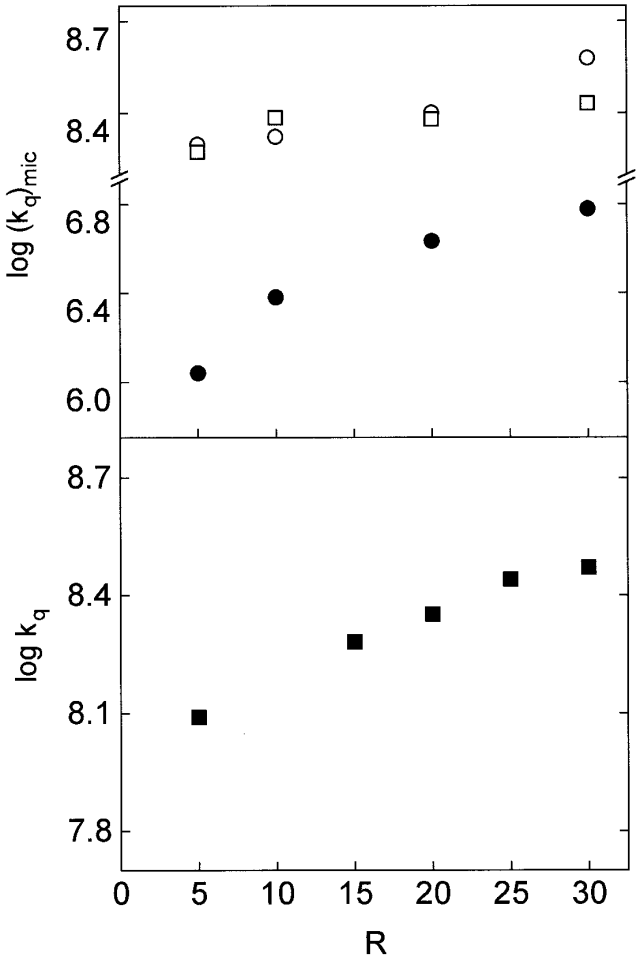

FIG. 1. Bulk and intramicellar quenching rate constants in 0.1 *M* AOT/heptane reverse micelles as a function of *R:* (■) quenching of PBTMA by 1,2-DMI, (●) quenching of PBTMA by indole, (○) quenching of PMTMA by indole and (□) quenching of PSA by indole.

TABLE 2

Quenching by Indole, Intramicellar Fluorescence Quenching Rate Constants in AOT 0.1 *M*/Heptane Reverse Micelles at 25°C and $R = 30$

	$(k_q)_{mic}/10^7\ M^{-1}\ s^{-1}$		
	PBTMA	PMTMA	PSA
AOT ($R = 30$)	0.60	38.0	27.0
Ethanol	3.8	420	260

TABLE 3

Quenching by L-Tryptophan, Intramicellar Fluorescence Quenching Rate Constants in AOT 0.1 *M*/Heptane Reverse Micelles at 25°C

	$(k_q)_{mic}/10^7\ M^{-1}\ s^{-1}$		
R	PBTMA	PMTMA	PSA
Water	210	380	270
10		6.5	
20		8.3	
30	2.6	16.4	18.7

II. Quenching by Tryptophan and Tryptamine

The quenching of the pyrene derivatives by the water-soluble indolic compounds, tryptophan and tryptamine, can also be analyzed in terms of the location of the donor–acceptor pair in the reverse micelle. Irrespective of the size of the water pool and the pH, most of the tryptophan molecules are localized at the interface (11). The same happens with tryptamine when the water pool is prepared with water at pH 3. Under these conditions all the tryptamine molecules are protonated and the indole moiety of tryptamine remains at the micellar interface (7). Furthermore, it can be considered that the tryptamine population is sensing a single microenvironment whose properties are almost invariant when *R* changes from 11 to 44 (7). As the pyrenic probes are localized at the interface, then both the probe and the quencher are completely incorporated to the micellar pseudophase. In this situation the experimental fluorescence decays start to deviate from the monoexponential behavior, and the decay curves were adjusted with Eq. [4] to obtain the pseudounimolecular intramicellar quenching rate constants k_{qm} (27–32),

$$I_{(t)} = I_{(0)}\exp(-k_0 t - \bar{n}\{1 - \exp[-k_{qm}t]\}), \qquad [4]$$

where I_0 is the fluorescence intensity at $t = 0$, k_0 is the inverse of the lifetime of the probe in the absence of quenchers, $\bar{n}$ the mean number of quenchers per micelle, and k_{qm} the pseudounimolecular intramicellar quenching rate constant. The values of k_{qm} were obtained by fitting the fluorescence decay curves to Eq. [4] for a number of quencher molecules per reverse micelle ($\bar{n}$) ranging from 2 to 12.

In order to compare the results in the reverse micelles with those in homogeneous solution, bimolecular rate constants inside the reverse micelles, instead of pseudounimolecular ones, are necessary. The $(k_q)_{mic}$ values were obtained by converting the unimolecular rate constants k_{qm} in bimolecular rate constants. This was done by assigning a volume to the micellar aggregate as described above for the quenchers partitioned between the interface and the *n*-heptane phase. In Tables 3 and 4 are presented the resulting values of $(k_q)_{mic}$, together with the bulk quenching rate constants in water. It can be observed that the rate constants are smaller than in water and that again the order is PSA ≅ PMTMA ≫ PBTMA. In the case of the quenching of PMTMA by tryptophan the rate constants increase with *R*.

III. Laser Flash Photolysis Experiments

In order to get information about the nature of the quenching process in the reverse micellar system, laser flash photolysis experiments were conducted. After 1 μs of the laser excitation at 337 nm, the transient spectra of PBTMA or PSA in the absence of quenchers showed the typical absorption due to triplet state of the pyrene derivative, with a maximum near 420 nm (33, 34), Figs. 2 and 3. The spectra in the presence of quencher show, as the only transient after the quenching process, the triplet of the pyrene derivatives. In contrast, similar experiments in homogeneous solvents present the characteristic absorption of pyrene radical anion as the main result of the quenching reaction (22). In the spectra in Figs. 2 and 3 the indole concentration is such that ca. 50% for PBTMA and 99% for PSA of the excited singlets are intercepted. However, the T–T absorption is larger than that expected according to the fraction of excited singlet states quenched.

DISCUSSION

The pyrenyl group of PBTMA and PMTMA is forming part of a detergent-like cationic probe. Due to electrostatic and hydrophobic interactions the probes are localized at the interface between the organic solvent and the water pool in the

TABLE 4

Quenching by Tryptamine, Intramicellar Fluorescence Quenching Rate Constants in AOT 0.1 *M*/Heptane Reverse Micelles at 25°C

	$(k_q)_{mic}/10^7\ M^{-1}\ s^{-1}$		
	PBTMA	PMTMA	PSA
AOT ($R = 30$)	4.7	20.5	20.0
Water	280	410	770

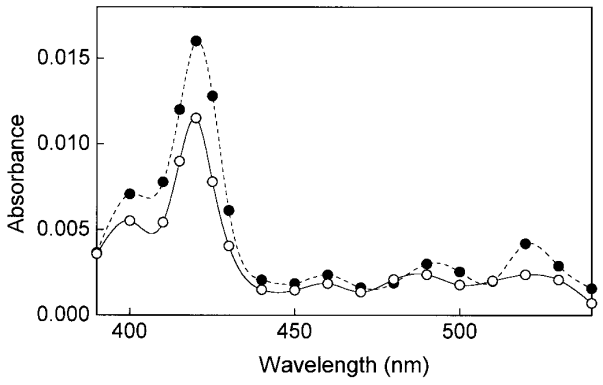

FIG. 2. Transient absorption spectra of PBTMA in 0.1 *M* AOT/heptane, $R = 20$, in the absence (●) and the presence (○) of indole 0.05 *M*, taken at 1 μs after the laser pulse.

reverse micellar system formed by the anionic surfactant AOT. In them the cationic head is anchored at the micellar surface while the pyrenyl moiety is located in the hydrophobic region of the surfactants (8, 26). The excitation and emission spectra of these probes were independent on the composition of the solution, and the fluorescence decay times were monoexponential, supporting that the excited molecules constitute a single and homogeneous population, as expected for probes totally incorporated to the micellar interface (8, 26). From the fluorescence behavior of exciplexes formed between PBTMA and PMTMA with dimethylaniline (DMA) in AOT reverse micelles, it was concluded that the pyrenyl group is located at different distances from the interface, depending on the length of the methylenic chain (25, 34). The position of the maximum of the band and the quantum yield of the exciplex emission were used to sense the interface polarity. It was reported that for PMTMA the location of the pyrenyl group is very close to the surfactant's polar heads and the water pool, whereas for PBTMA it is immersed into the surfactant tails in a less polar region of the micellar interface.

Although PSA bears the same charge as the detergent molecules it is also believed to be located mainly at the interface (8, 26, 35), most probably co-micellizing with the surfactant molecules. Recently, it was reported that at $R \geq 10$, PSA starts to move to the water pool of the reverse micelle, and it was estimated that at $R = 30$, ca. 20% of the PSA is in the water pool (35). However, our quenching data show that the behavior of PSA is very similar to that observed for PMTMA, which is a probe assumed to be totally incorporated into the AOT interface.

I. Quenching by Neutral Indoles

It is well established that in AOT reverse micelles 1,2-DMI is in the organic phase (11). In the same way 1-MI may be supposed to reside mainly in the *n*-heptane. From the k_q values in Table 1 it is observed that the quenching process is dependent on the location of the pyrene derivative in the interface. Moreover, the Stern–Volmer plots from stationary and dynamic fluorescence measurements were coincident and linear, indicating the nonexistence of a static quenching component, and that the rates of entrance and exit of the quencher in the micelles are very high. Since it is known that the quenching of pyrene and its derivatives by indole depends upon the solvent polarity (18, 19, 21) the observed differences in the k_q values in Table 1 can be, at first, related to polarity effects of the microenvironment where the quenching process is taking place. It can be observed that the quenching rate constants in AOT solutions for these indole derivatives are lower than those in ethanol. The difference is more pronounced for PBTMA. This may be due to the high sensitivity of the quenching of PBTMA by indole to the solvent dielectric constant, since in homogeneous solvents it increases by more than one order of magnitude on going from ethanol to water (36).

The bulk quenching rate constants, k_q, of PBTMA by 1,2-DMI increase with *R*, Fig. 1. This variation with *R* may be explained if it is assumed that, as the size of the water pool increases, the change in the curvature of the interface 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. Therefore, the quenching rate constant increases as a consequence of the increment of the polarity of the micellar interface. These results are in line with the results on the exciplex emission of the system PBTMA–DMA, from which it was concluded that the polarity at the interface increases with *R* (25). However, the variation in k_q for the quenching of PBTMA by 1,2-DMI is smaller than the change in the intramicellar quenching rate constant $(k_q)_{mic}$ for the quenching by indole, Fig. 1. The difference can be assigned to the larger donor capacity of 1,2-DMI, than indole, as evidenced by the redox potentials of indole and its derivatives (37).

In the quenching of PMTMA and PSA by indole, the intramicellar quenching rate constants $(k_q)_{mic}$ at $R = 30$ are one order of magnitude smaller than those in homogeneous solvents, Table 2. Since in homogeneous solvents the quenching

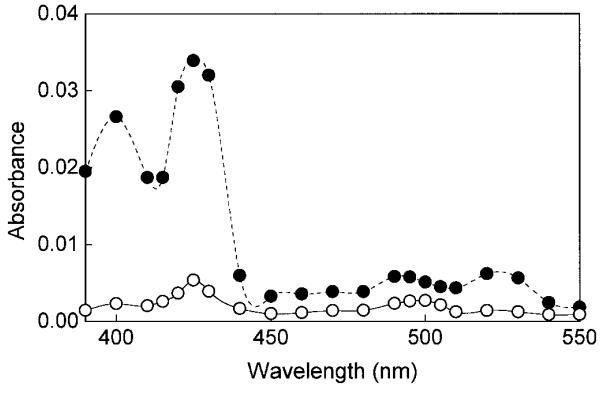

FIG. 3. Transient absorption spectra of PSA in 0.1 *M* AOT/heptane, $R = 20$, in the absence (●) and the presence (○) of indole 0.05 *M*, taken at 1 μs after the laser pulse.

is diffusion controlled (36), the process at the interface can also be assumed to be near the diffusional limit. Therefore, the lower rate constants in AOT reverse micelles can be associated with a higher viscosity of the interface that decreases the encounter probability between the reactants. In Fig. 1 it can be seen that for these systems $(k_q)_{mic}$ present a small increment with *R*. This effect can be ascribed to a diminution of the interface viscosity with *R* (38, 39, 40). A similar dependence of $(k_q)_{mic}$ on the water content was obtained for the quenching of PMTMA by fumaronitrile (8), a hydrophilic quencher, and also for the quenching of pyrenic probes by TEMPOL, a nitroxide quencher similarly partitioned between the interface and the organic phase (12). This interpretation is supported by the values reported by Zinsli (38) and Hasegawa *et al.* (39, 40) for the viscosities of the AOT reverse micelle's interface. Zinsli's results were derived from time-resolved anisotropy measurements and computer simulation of a model in which the probe moves in the micellar core and is quenched at the interface. The data show a decrease in the viscosity from 24 ± 4 cP at $R = 9$ to 5 ± 2 cP at $R = 30$. The data of Hasegawa *et al.* were obtained from fluorescence quantum yield measurements of auramine-O in the reverse micelles and comparison with the fluorescence quantum yield in water–glycerol mixtures. This set of data gives viscosities ranging from around 25 cP at $R = 10$ to 15 cP at $R = 30$.

II. Quenching by Tryptophan and Tryptamine

The quenching of PSA and PMTMA by tryptophan and tryptamine may be also explained by a higher viscosity of the interface. For these systems the rate constants in water are close to the diffusion limit, Tables 3 and 4. Furthermore, it was reported that the quenching of pyrene by tryptophan in ethanol–water mixtures is diffusionally controlled (19). On the other hand, in the reverse micellar system it can be observed that the rate constants for the quenching of PSA and PMTMA by tryptophan and tryptamine at $R = 30$ are similar, and much lower than in water. This effect can be explained by a very low mobility of the quencher and probe caused by a very rigid structure of the interface and/or by their binding to the polar heads of AOT. For the quenching of PMTMA by tryptophan the $(k_q)_{mic}$ values increase with *R*, indicating a reduction of the rigidity of the micellar interface as the size of the aggregate increases, as discussed above.

III. Laser Flash Photolysis Results

The results from laser flash photolysis experiments are in agreement with the lower mobility of the reactants in the micellar interface. While in the photoinduced electron transfer reaction in polar solvents between pyrene and indole free radicals ions are observed (22), in the reverse micellar system only the triplet state of the pyrene derivatives appears as a transient species, Figs. 2 and 3. This is in agreement with a very low rate constant for the escape of the radical ions. From the reported local viscosity (38) and dielectric constant (25) of the AOT interface, the escape rate constant can be estimated as $2–3 \times 10^6\ s^{-1}$ from Eigen's formula (41). It is known that for the Py-indole system the back-electron-transfer to triplet k_b, is ca. $5 \times 10^8\ s^{-1}$, independent of the solvent polarity (21). Therefore, assuming a similar value in the reverse micellar solution, it is reasonable to expect that free ions are not observed.

In conclusion, the quenching by indolic compounds of pyrenic probes anchored to the AOT reverse micelles' interface can be explained by taking into account the local properties of the interface, such us polarity and viscosity. Moreover, the observed trend in the rate constants when *R* is varied is in line with the reported changes in micropolarity and viscosity of the interface. From a comparison of the triplet–triplet absorption of the pyrene derivatives in the absence and the presence of the quenchers it may be concluded that in these systems the main result of the quenching process is the formation of the excited triplet of the probe. From the point of view of the control of the kinetics and the product distribution of photochemical reactions in a reverse micellar system, the present results show how 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. In the particular case of AOT reverse micelles, the interface plays a predominant role in preventing charge separation in photoinduced electron transfer reactions. This effect can preclude the employment of this media in the production of energy-rich species.

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