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Exciplex Formation between Pyrene Derivatives and *N,N*-Dimethylaniline in Aerosol OT Reversed Micelles

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The fluorescence spectra, fluorescence decay times, and the fluorescence quantum yield of the exciplexes formed between several fluorescent probes containing the pyrene chromophore with dimethylaniline were studied in reversed micellar solutions made from sodium bis(2-ethylhexyl)sulfosuccinate (AOT) and water in *n*-heptane. The pyrene probes used were 1-methylpyrene (1-MP), (1-pyrenylmethyl)-trimethylammonium iodide (PMTMA), (4-(1-pyrenyl)butyl)trimethylammonium bromide (PBTMA), and (11-(1-pyrenyl)undecyl)trimethylammonium iodide (PUTMA). For the detergent-like probes, which are bound to the micellar interface, the fluorescent properties are dependent on the length of the aliphatic chain of the probe and the water to AOT ratio in the reversed micelles (R). The fluorescence emission maxima shift to the red and the fluorescence quantum yields and fluorescence decay times decrease with the water content of the micelle. For probes like 1-MP which are not bound to the interface, the emission maxima shift to the blue with an increase in R. The PBTMA–DMA exciplex was also studied in *n*-decane solutions.

Introduction

Among the amphiphiles capable of forming inverted micelles, sodium bis(2-ethylhexyl)sulfosuccinate (AOT) has received much attention in the last years. It has the ability to solubilize relatively large amounts of water in various organic solvents producing transparent microemulsions. The peculiarity of these microemulsions lies in their molecular heterogeneity caused by the amphiphilic nature of the surfactant which resides on an interface between the practically immiscible water and organic solvent. Reversed micelles consist of at least three different compartments in which small probe molecules can be solubilized: an internal aqueous microphase (water pool), the interface of the surfactant molecules, and the external organic phase.[1-3] Therefore, these systems are suitable media for processes that involve hydrophobic and hydrophilic reactants.

Questions of interest relative to AOT-inverted micelles are the structural organization of the surfactant layer[4] and its relation to percolation processes in microemulsions[5,6] and the dynamic properties of molecules present in the different compartments of the micelles including the intercompartamental rate of exchange.[7-9] Also of current interest are the dielectric properties of microemulsions[10] and the polarity of the micellar interface.[11,12]

Fluorescence techniques have been widely used by different authors to investigate the properties of the aqueous core and the interface of AOT reversed micelles and to determine the position of fluorescent probes and quenchers.[13-15]

Exciplexes have been studied extensively in homogeneous solutions. They are characterized by large dipole moment, and their fluorescence properties are strongly dependent on the environment polarity. Exciplex formation was proposed as a good method to obtain information on the average localization site of probes in reversed micelles.[16] Exciplexes were also studied in liposomes,[17] micelles,[18,19] and water in oil microemulsions.[20]

A simple but well-known electron transfer system forming exciplexes is pyrene–*N,N*-dimethylaniline (DMA). Photoexcitation of pyrene in the presence of DMA leads to the formation of exciplexes in low polarity media[21,22] and radical ions in polar solvents[22] and organized systems.[17,18,23]

When the pyrenyl group is forming part of a detergent-like probe, which can be bound to the AOT micellar interface,[24,25] it is possible to study the properties of the exciplex at different distances from the interface changing the alkylic chain length of the probe.[16] This makes it

(1) Fendler, H. J. *Membrane Mimetic Chemistry*; Wiley-Interscience: New York, 1982.
(2) Luisi, P. L., Straub, B. E., Eds. *Reverse Micelles*; Plenum: New York, 1984.
(3) Encinas, M. V.; Lissi, E. H. *Chem. Phys. Lett.* **1986**, *132*, 153.
(4) Hou, M. J.; Shah, D. O. *Langmuir* **1987**, *3*, 1086.
(5) Borkovec, M.; Eicke, H. F.; Hammerich, H.; Das Gupta, B. *J. Phys. Chem.* **1988**, *92*, 206.
(6) Jada, A.; Lang, J.; Zana, R. *J. Phys. Chem.* **1989**, *93*, 10.
(7) Fletcher, P. D. I.; Robinson, B. H. *Ber. Bunsen-Ges. Phys. Chem.* **1981**, *85*, 863.
(8) Fletcher, P. D. I.; Howe, A. M.; Robinson, P. J. *J. Chem. Soc., Faraday Trans.* **1987**, *83*, 985.
(9) Lang, J.; Jada, A.; Malliaris, A. *J. Phys. Chem.* **1988**, *92*, 1946.
(10) Middleton, M. A.; Schechter, R. S.; Johnston, K. P. *Langmuir* **1990**, *6*, 920.
(11) Belletete, M.; Lachapelle, M.; Durocher, G. *J. Phys. Chem.* **1990**, *94*, 5337.
(12) Lay, M. B.; Drummond, C. J.; Thistlehwaite, P. J.; Grieser, F. J. *J. Colloid Interface Sci.* **1989**, *128*, 602.
(13) Kalyanasundaram, K. *Photochemistry in Microheterogeneous Systems*; Academic Press: Boca Raton, FL, 1987.
(14) Lissi, E. A.; Encinas, M. V.; Bertolotti, S. G.; Cosa, J. J.; Previtali, C. M. *Photochem. Photobiol.* **1990**, *51*, 53.
(15) Encinas, M. V.; Lissi, E. A.; Bertolotti, S. G.; Cosa, J. J.; Previtali, C. M. *Photochem. Photobiol.* **1990**, *52*, 981.
(16) Geladé, E.; Boens, N.; De Schryver, F. C. *J. Am. Chem. Soc.* **1982**, *104*, 6388.
(17) Waka, Y.; Mataga, N.; Tanaka, F. *Photochem. Photobiol.* **1980**, *32*, 335.
(18) Katusin-Razem, B.; Wong, M.; Thomas, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 1679.
(19) Waka, Y.; Hamamoto, K.; Mataga, N. *Chem. Phys. Lett.* **1978**, *53*, 242.
(20) Atik, S. S.; Thomas, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4367.
(21) Mataga, N.; Okada, T.; Yamamoto, N. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2562. Beens, H.; Knibbe, H.; Weller, A. *J. Chem. Phys.* **1967**, *47*, 1183.
(22) Hirata, Y.; Kanda, Y.; Mataga, N. *J. Phys. Chem.* **1983**, *87*, 1659. Potashnik, R.; Goldschmidt, C. R.; Ottolenghi, M.; Weller, A. *J. Chem. Phys.* **1971**, *55*, 5344.
(23) Atik, S. S.; Thomas, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 3550.
(24) Sáez, M.; Abuin, E. A.; Lissi, E. A. *Langmuir* **1989**, *5*, 942.
(25) Encinas, M. V.; Lissi, E. A.; Previtali, C. M.; Cosa, J. J. *Langmuir* **1989**, *5*, 805.

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possible to obtain information on the microenvironment sensed by the pyrene–DMA exciplex at different distances from the water pool.

In the present paper we wish to report a study of the fluorescence quenching of 1-methylpyrene (1-MP), (1-pyrenylmethyl)trimethylammonium iodide (PMTMA), (4-(1-pyrenyl)butyl)trimethylammonium bromide (PBTMA), and (11-(1-pyrenyl)undecyl)trimethylammonium iodide (PUTMA) by DMA in reversed micelle solutions of AOT. The effects of the AOT concentration and the water/AOT ratio on the quenching rate constants and the exciplex fluorescence properties were studied. For the special case of PBTMA, the effect of the organic dispersing solvent and the temperature were also studied. The results indicate that the microenvironment sensed by the exciplex formed between PBTMA and DMA behaves similarly when the solvent is *n*-heptane at room temperature or when it is *n*-decane at higher temperatures under conditions where percolative conduction has been reported.[6,10]

Experimental Section

Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) was purchased from Sigma and was dried under vacuum and used without further purification.

(1-Pyrenylmethyl)trimethylammonium iodide (PMTMA), (4-(1-pyrenyl)butyl)trimethylammonium bromide (PBTMA), and (11-(1-pyrenyl)undecyl)trimethylammonium iodide (PUTMA) were Molecular Probes products and employed as received. Pyrene (Aldrich) and 1-Methylpyrene (1-MP) were recrystallized several times. Their fluorescence lifetimes in AOT solutions were in agreement with reported values.[24]

Dimethylaniline (DMA), Merck, was distilled under vacuum immediately before to use.

Heptane, Sintorgan HPLC grade, and decane, Aldrich, 99%, were used as received.

All experiments were performed under controlled temperature in solutions deareated by nitrogen bubbling. Care was taken to avoid solvent and/or water evaporation. The AOT to probe ratios were always large enough to avoid multiple probe occupancy. Typically, 5×10^{-6} M solutions of the probe were employed for fluorescence studies.

Fluorescence spectra were obtained in an Aminco Bowman spectrofluorometer. In the case of the PMTMA–DMA exciplex, the emission spectrum was obtained with minimum excitation light intensity in order to avoid the interference of an inidentified product produced by photolysis of the solutions.

The fluorescent decay times and fluorescence quantum yields of the exciplexes were measured in solutions containing 5×10^{-6} M of the probe and 8×10^{-2} M of DMA. Here the fluorescence intensity of the pyrene derivative was reduced to less than 5% of the value in the absence of DMA. Under these conditions the long tail of the exciplex fluorescence decay curve could be fit to a single exponential. The decay curves were obtained at 515 nm and their analysis started 30 ns after the end of the laser pulse.

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 54200 oscilloscope. It was then transferred via an IEEE interface to an PC-XT computer, where it was processed. The signal to noise ratio was compatible to analyze the decay curves just over a 1.5 decades range. The estimated error in the decay times was ∓3% or ∓0.5 ns, whichever is greater.

The fluorescence quantum yields were measured relative to quinine bisulfate in 0.1 N sulfuric acid as standard.

Results and Discussion

Fluorescence of DMA in AOT Reversed Micelles. The fluorescence spectra of DMA in *n*-heptane, ethyl acetate, methanol, and reversed micelles of AOT in *n*-heptane are shown in Figure 1. A red shift of the emission

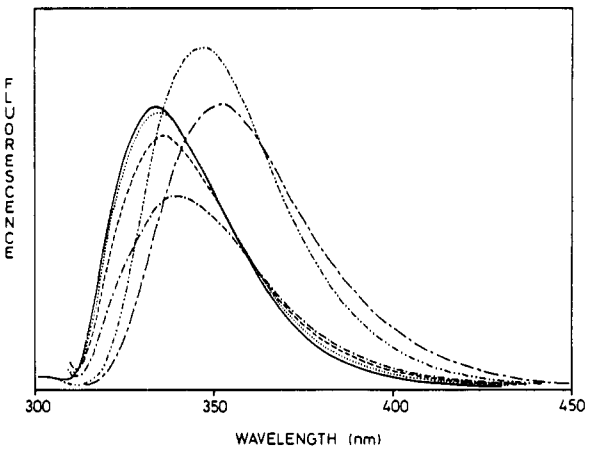

Figure 1. Fluorescence emission spectra of dimethylaniline in different solvents: (——) *n*-heptane; (· · ·) AOT 0.05 M, $R = 20$; (- - -) AOT 0.2 M, $R = 20$; (- · -) AOT 0.5 M, $R = 20$; (- · · -) ethyl acetate; (– – –) methanol.

maximum can be observed with the solvent polarity. Also red shifts in the spectra are observed in the solutions containing AOT when the concentration of the surfactant is increased. This is an indication that DMA is partitioned between *n*-heptane and the reversed micelles. We do not observe changes in the fluorescence spectra of DMA by changing R at a given concentration of AOT. This result was similar to that observed with indole in AOT reversed micelles.[14] The fluorescence intensity of DMA was the same when the water pool was prepared with pure water or a Tris buffered solution, indicating that no protonation of DMA at the interface occurs. The above result confirms the partition of DMA between the organic phase and the interface of the reversed micelle.

PMTMA, PBTMA, and PUTMA in AOT–Heptane Solutions. The absorption and emission spectra of PMTMA, PBTMA, and PUTMA coincide with literature reports. Their fluorescence lifetimes agreed with previously reported results in AOT solutions.[24]

The fluorescence decays of PMTMA, PBTMA, and PUTMA in the absence of DMA were fit, within experimental error, by a single exponential at all the AOT concentrations studied. This means that the excited molecules constitute a single and homogeneous population, as expected for probes which are totally incorporated to the interface of the reversed micelles.[24,25] The absorption spectra of the probes bound to the interface indicate no measurable ground-state interactions with DMA.

The decay of the probes, obtained at 380 nm, in the presence of DMA also appears as a single exponential. From these measurements the apparent quenching rate constants could be obtained from plots of $1/\tau$ versus [DMA] according to

$$1/\tau = 1/\tau^\circ + k_q[\mathrm{DMA}] \qquad (\mathrm{I})$$

where τ° and τ are the fluorescence decay times of the probes in the absence and presence of DMA, respectively. Here [DMA] refers to the bulk concentration. In Table I are given the apparent quenching rate constants of the pyrenic probes by DMA at several AOT concentrations and different values of R. Plots of I°/I were also linear, indicating that the quencher exchange between the micelle and the oil phase is fast and/or the number of quenchers per micelle is large.[26] Similar k_q values were obtained from I°/I or τ°/τ plots.

(26) Encinas, M. V.; Lissi, E. A. *Chem. Phys. Lett.* **1986**, *132*, 545.

Table I. Fluorescence Quenching Rate Constants of the Cationic Pyrene Probes by *N,N*-Dimethylaniline and Fluorescence Parameters of the Exciplexes in *n*-Heptane–AOT Solutions at 25 °C[a]

	PMTMA			PBTMA				PUTMA			
R	k_q	λ	ϕ	k_q	λ	τ	ϕ	k_q	λ	τ	ϕ
					AOT 0.05 M						
0		515	<0.01		495	110	0.180		488	118	0.233
5	3.68			2.28	512	65	0.116	2.72	505	63	0.112
10	3.93			2.27	520	33	0.063	2.99	515	41	0.074
20	3.45			2.21	530	19	0.021	3.37	523	25	0.050
40	3.58			1.92	540	13	0.015	3.17	535	18	0.042
					AOT 0.1 M						
0		515	<0.01		495	109	0.181		488	112	0.213
5	3.50			2.53	515	51	0.076	2.84	507	57	0.091
10	3.67			2.45	525	30	0.038	2.94	517	37	0.062
20	3.49			2.21	533	17	0.021	3.28	525	24	0.040
40	3.27			2.20	540	13	0.017	3.79	535	18	0.027
					AOT 0.2 M						
0		516	<0.01		495	109	0.193		487	117	0.217
5	3.57			2.20	515	51	0.070	2.87	508	56	0.069
10	4.04			2.21	525	26	0.036	3.23	517	36	0.059
20	3.58			2.29	535	17	0.023	3.40	525	25	0.036
40	3.49			2.25	540	13	0.016	3.79	535	19	0.026

[a] Key: k_q, fluorescence quenching rate constants × 10^{-9} M^{-1} s^{-1}; τ, fluorescence lifetimes in ns; λ, emission maxima in nm; ϕ, fluorescence quantum yields.

From Table I it can be observed that for the three probes studied, at a given R, the quenching rate constants are nearly independent of the AOT concentration within the experimental error. For PMTMA and PBTMA it seems that there is not a definitive trend when increasing R. However, the quenching rate constants for PUTMA are larger as R increases.

The quenching rate constants are not much different for the three probes studied, although larger rate constants were observed for PMTMA. However, in a few cases, especially at large R, the rate constants for PUTMA exceed those for PMTMA. In all situations the smaller rate constants were those obtained for PBTMA. In general the rate constants follow the order PMTMA ≥ PUTMA > PBTMA.

The fluorescence quenching of the three probes by DMA is accompanied by the characteristic emission of the exciplex pyrene–DMA. The fluorescence excitation spectra observed at the monomer or exciplex emission maxima were coincident, confirming in this way the lack of ground-state associations between the probes and DMA. In Figure 2 are shown the fluorescence spectra of PBTMA in the presence of DMA at different water/AOT ratios. It can be observed that fluorescence quantum yield of the exciplex is strongly dependent on the amount of water incorporated to the reversed micelle. A similar effect has been previously noted in the study of exciplexes of naphthalene derivatives with triethylamine in dodecylammonium propionate reversed micelles.[16]

In Figure 2 it can also be observed that the quenching of the exciplex fluorescence is accompanied with a red shift of the spectrum. Similar results were obtained when PUTMA was the probe employed. However, when PMTMA was used, the exciplex can only be detected at low R and with a fluorescence quantum yield lower than 0.01. At R = 10 the exciplex could not be observed.

The fluorescence decay of the exciplexes appears monoexponential under our experimental conditions. This is contrasted with the well-known biexponential decay in homogeneous solutions. The single exponential behavior here observed can be due to two factors, that we measured the slower region of the decay (see Experimental Section) and/or that the back dissociation of the exciplex to the locally excited state is of the order of 1 × 10^6 s^{-1}, to be compared with 1.8 × 10^7 s^{-1} for the system pyrene–DMA in cyclohexane.[27]

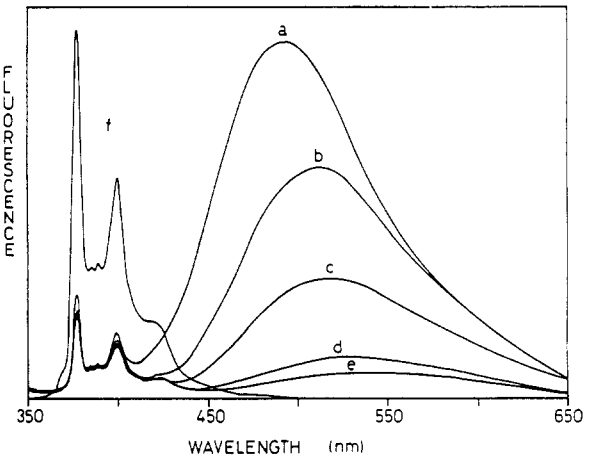

Figure 2. Fluorescence emission spectra of 5 × 10^{-6} M (1-pyrenylbutyl)trimethylammonium bromide in the absence and in the presence of 0.08 M dimethylaniline at different water/AOT ratios, in *n*-heptane–AOT 0.05 M solutions: (a) R = 0; (b) R = 5; (c) R = 10; (d) R = 20; (e) R = 40; (f) pyrene probe in the absence of dimethylaniline on a 3 times larger scale.

The fluorescence maxima, decay time, and quantum yield of PMTMA, PBTMA, and PUTMA exciplexes are collected in Table I. It can be seen that the emission maximum of the exciplex formed by the probe with the longer aliphatic chain is more blue shifted, the decay times are longer, and the quantum yields are greater at all AOT concentrations. These results suggest that the exciplexes are sensing different microenvironments which are more polar as the methylenic chain becomes shorter. When the different parameters are analyzed for a given probe as a function of the water content of the micelle, in general the emission maximum of the exciplex shifts to the red and the fluorescence decay times and quantum yields decrease as R increases.

An understanding of the solvent polarity effect on the emission spectrum of the exciplexes can be obtained from a comparison with the solvent effect on an exciplex model

(27) Froehlich, P.; Wehry, E. L. In *Modern Fluorescence Spectroscopy*; Wehry, E. L., Ed.; Plenun Press: New York, 1976; Vol 2, p 379.

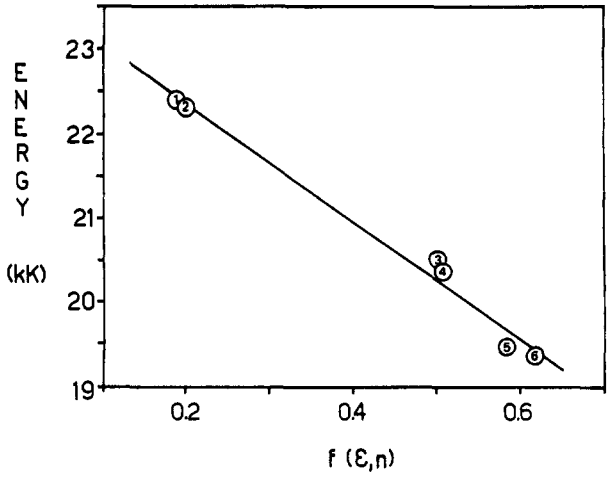

Figure 3. Solvatochromic shift of the 1-methylpyrene–dimethylaniline exciplex emission spectrum in neat solvents: E, energy of the band at λ_{max}; $F(\epsilon,n) = (2[(\epsilon - 1)/(2\epsilon + 1)] - [(n^2 - 1)/(2n^2 + 1)])$; (1) n-heptane, (2) n-decane, (3) ethyl ether, (4) chloroform, (5) ethyl acetate, (6) tetrahydrofuran.

compound. To this purpose 1-methylpyrene–DMA exciplex was selected as the model compound. The effect of solvent polarity is normally evaluated by plotting the fluorescence maxima against the following equation[28]

$$\nu \cong \nu_0 - \frac{2\mu^2}{hc\alpha^3}\left(2\left(\frac{\epsilon - 1}{2\epsilon + 1}\right) - \left(\frac{n^2 - 1}{2n^2 + 1}\right)\right) \qquad \text{(II)}$$

where ν and ν_0 are the emission maximum of the exciplex in solution and in vacuum, μ is the dipole moment of the exciplex, α is the radius of the spherical cavity occupied by the exciplex, ϵ is the static dielectric constant of the solvent, and n is its refraction index. h and c are Planck's constant and the light velocity, respectively. In Figure 3 the energy of the emission maximum of the 1-methylpyrene–DMA exciplex in pure solvents is plotted versus the brackets of equation II, and a reasonable linearity is observed. If we wish to correlate the emission maximum of the exciplexes formed by the pyrenic probes with DMA, in a micellar medium, with a certain ϵ value, we must assume that the molecular radius and the dipole moment of these exciplexes are comparable with that of the 1-methylpyrene–DMA exciplex. Also we must assume that the refraction index of the reversed micelles is between 1.3524 and 1.4459, the extreme values of the refraction index of the solvents employed which correspond to diethyl ether and chloroform, respectively.

When ν_{max} of the fluorescence band of PBTMA–DMA exciplex is compared with the result for the exciplex model compound (Figure 3), it is possible to assign a dielectric constant of around 4–5 at $R = 0$, 9–10 at $R = 10$, and about 14–16 at larger R, assuming that the refraction index of the micelle is the average refraction index of the solvents employed. The results are nearly independent on AOT concentration. Except at low R values, where the quantum yield of the exciplex is relatively large, accurate determinations of ν_{max} are difficult because the exciplex band is very broad. The dielectric constant sensed by the probe increases rapidly at low R and then more slightly at larger R. This result compares well with the recently reported polarity of the AOT interface using a 3*H*-indole derivative and the concept of preferential solvation,[11] where a plateau is reached at $R = 12$. However, the dielectric constants sensed by the pyrenyl probes are larger than those sensed by the indolic probe. The exciplex formed between PUTMA and DMA senses a slightly less polarity than that sensed by the exciplex PBTMA–DMA at the same water/AOT ratio.

(28) Mataga, N.; Ottolenghi, M. In *Molecular Association*; Foster, R., Ed.; Academic Press: London, 1979; Chapter 1.

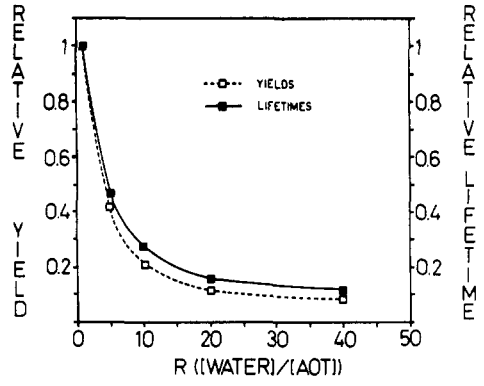

Figure 4. Relative fluorescence lifetimes and quantum yields of the (1-pyrenylbutyl)trimethylammonium bromide–dimethylaniline exciplex in n-heptane–AOT 0.1 M solutions at different water/AOT ratios.

Exciplex fluorescence quantum yield and fluorescence decay times can also provide information about the reversed micelles. In Figure 4 the fluorescence decay times of PBTMA at the different values of R, divided by the fluorescence decay time at $R = 0$, are plotted as a function of R. Two slopes can be observed in this plot, one of them steep at low R and the other slight at larger R with a transition around $R = 10$. Similar results were obtained by plotting the relative quantum yields. The same behavior was observed for PUTMA indicating that both probes are sensing not very different microenvironments.

The above results are in good agreement with the accepted model of reversed micelles of AOT, where the water pool is formed at approximately $R = 10$. However, the fluoroescence quantum yields and the fluorescence decay times at $R = 40$ are at least 25% lower than those at $R = 20$ for both PUTMA and PBTMA at all AOT concentrations (Table I). This can be associated with a significantly larger polarity at the larger R. In going from $R = 20$ to $R = 40$ the reversed micelles are increasing their aggregation number and the radius of the water pool. This results in a decrease of the curvature radius of the interface and an increase of the area occupied by each AOT molecule.[9] Therefore the larger polarities that are sensing the exciplexes can be associated to the above changes. The quenching with increasing R could be explained if it is assumed that the interface is more open and more water molecules can reach the region where the exciplex is found. An alternative explanation is to suppose that increasing the total water content would expose the exciplex to a higher mean polarity due to micellar exchange. However if this should be the case, a decrease of the exciplex emission quantum yield and lifetime would be expected with increasing AOT concentration at a given R. It can be seen from Table I that for the three AOT concentrations at $R = 20$ or 40 the parameters are unchanged for the case of PBTMA and only a change can be observed for PUTMA at the lower concentrations. Therefore in any case this explanation cannot be valid to explain all the observations.

Pyrene and 1-Methylpyrene in AOT–Heptane Solutions. For 1-methylpyrene (1MP), the model compound soluble in nonpolar solvents, the quenching rate constants by DMA are reported in Table II. It can be observed that the rate constants are not controlled by diffusion.

In n-heptane solutions the quenching is accompanied with the formation of the longer wavelength broad band

Table II. Fluorescence Parameters of 1-Methylpyrene-*N,N*-Dimethylaniline Exciplex in *n*-Heptane-AOT Solutions at 25 °C

	R	λ_{max}, nm	τ_{exc},[a] ns	ϕ	$k_q \times 10^{-9}$ M^{-1} s^{-1}
AOT 0.05 M	0	460	107	0.187	
	5	453	*	0.140	
	10	450	*	0.117	
	20	446	*	0.102	
	40	445	59	0.128	
AOT 0.1 M	0	474	102	0.228	
	5	471	*	0.140	
	10	452	*	0.110	
	20	450	*	0.102	
	40	445	46	0.105	
AOT 0.2 M	0	481	118	0.237	
	5	480	*	0.120	
	10	465	*	0.082	
	20	452	*	0.063	
	40	447	30	0.065	
n-heptane		445	109	0.277	0.34
methanol					5.00

[a] Asterisk indicates nonexponential decay.

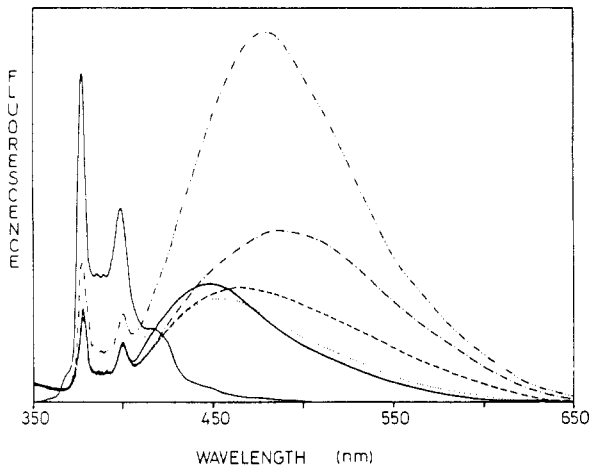

Figure 5. Fluorescence emission spectra of 5×10^{-6} M 1-methylpyrene in the absence and in the presence of 0.08 M dimethylaniline at different water/AOT ratios, in *n*-heptane-AOT 0.2 M solutions: (——) $R = 40$; (· · ·) $R = 20$; (- - -) $R = 10$; (- · -) $R = 5$; (- · · -) $R = 0$. On the left is shown the spectrum of 1-methylpyrene in the absence of dimethylaniline on a 3 times larger scale.

of the exciplex. This exciplex was not observed in polar solvents like methanol.

In AOT solutions, the quenching of 1MP is also accompanied by the apparition of the exciplex fluorescence band. This fluorescence band was also quenched by the addition of water to the solutions. However, the fluorescence spectra of 1MP-DMA exciplex in AOT solutions show several peculiarities as shown in Figure 5. At a given AOT concentration the emission maximum and the quantum yield of the exciplex are strongly dependent on R. An increase in the amount of water in the microemulsion produces a blue shift together with a narrowing of the spectrum. At the highest values of R the spectrum is very similar to that observed in *n*-heptane. This result is the opposite to that observed for the PBTMA and PUTMA-DMA exciplexes, where the exciplex spectrum was red shifted as R increased, Table II.

The emission spectrum of the exciplex also depends on the AOT concentration. An increase in the concentration of AOT shifts the exciplex spectrum to the red; this effect is more evident at low R, Table II.

The fluorescence spectra of the exciplexes formed between 1MP with DMA can be interpreted in terms of

Table III. Fluorescence Quenching Rate Constants of (1-Pyrenylbutyl)trimethylammonium Bromide by Dimethylaniline, Fluorescence Lifetimes, Fluorescence Quantum Yields, and Emission Maxima of the (1-Pyrenylbutyl)trimethylammonium Bromide-Dimethylaniline Exciplex in *n*-Decane-0.2 M AOT Solutions at 25 °C

R	$k_q \times 10^{-9}$ M^{-1} s^{-1}	λ_{max}, nm	τ_{exc}, ns	ϕ
0		500	126	0.134
5	1.6	520	56	0.047
10	1.6	530	30	0.024
20	1.7	540	21	0.013
25		543	20	0.012
30		545	18	0.012
40	1.7	545	16	0.011

exciplex formation in both the interface and the organic phase simultaneously. As the amount of water increases, the exciplex formed in the interface is quenched due to the larger dielectric constant, but the exciplex formed in the organic solvent remains almost unquenched. This can explain the blue shift of the spectrum and its narrowing at a given AOT concentration. The red shift of the exciplex fluorescence spectrum when the AOT concentration increases, at a given R, can be explained in terms of the 1MP fraction associated to the interface. The amount of 1MP associated to the interface increases with the concentration of AOT, therefore the spectrum resembles more and more the spectrum observed near the interface, which can be described by the spectrum of the exciplexes formed by PBTMA and PUTMA.

At $R = 40$, where supposedly most of the exciplexes associated with the micellar interface are quenched, the observed spectrum can be ascribed to the exciplex formed in the organic phase. However at this R, the fluorescence quantum yield of the exciplex decreases when the AOT concentration increases, indicating that it depends on the amount of dispersed phase. At $R = 40$, the exciplex fluorescence decay times are also dependent on the AOT concentration, Table II. This is an indication that the exciplex which is resident in the organic phase is quenched by the reversed micelles mostly in a dynamic way. A plot of $1/\tau$ versus the AOT concentration at $R = 40$, according to eq I, results in a rate constant of 1.2×10^8 M^{-1} s^{-1} for the quenching of the exciplex in the organic phase by AOT at this R.

The exciplex pyrene-DMA was also studied and similar results were observed, indicating that pyrene is also partitioned between the interface and the organic solvent.

PBTMA in AOT-*n*-Decane. Recently, Middleton et al.[10] reported that the changes in the bulk dielectric constant of AOT-water solutions in *n*-decane parallel the changes in the electric conductivity of the solutions as the temperature is increased. The dielectric constant changes suddenly from 4-5 at 25 °C to 25-30 at 45 °C, and a percolation threshold was observed at 40 °C for 0.2 M AOT solutions at $R = 25$. In order to check if the exciplex-forming process is sensible to these changes, we also studied the quenching of PBTMA by DMA in AOT-*n*-decane solutions.

The fluorescence quenching rate constants of PBTMA by DMA in AOT-0.2 M decane solutions are given in Table III. It can be seen that they are approximately 40% lower than those obtained in *n*-heptane, which can be explained by a viscosity effect. Also they are almost invariant with the amount of water contained in the reversed micelle. Again in this solvent the fluorescence quenching is accompanied with the formation of the PBTMA-DMA

exciplex. The fluorescence quantum yield of this exciplex also decreases with the addition of water to the AOT solution. The relative changes observed in fluorescence quantum yields, decay times, and position of the fluorescence maximum as R increases are very similar to those observed in n-heptane solutions and are shown in Table III. When the fluorescence spectra of the exciplex formed by PBTMA and DMA was studied as a function of temperature, at $R = 25$, the position of the fluorescence maximum was independent of the temperature in the range 20–50 °C. This may be an indication that the exciplex is not sensing the changes observed by Middleton in the bulk dielectric constant.

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