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Interface Effect on the Properties of Exciplexes Formed between Pyrene Derivatives and *N,N*-Dimethylaniline in Reversed Micelles

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The fluorescence spectra and fluorescence quantum yields of the exciplexes formed between *N,N*-dimethylaniline (DMA) and several fluorescent probes containing the pyrene chromophore were studied in reversed micellar solutions. The solutions were made from sodium bis(2-ethylhexyl) sulfosuccinate (AOT) or benzylhexadecyldimethylammonium chloride (BHDC), water, and benzene. The probes used were 1-methylpyrene (MP) in AOT and BHDC, [4-(1-pyrenyl)butyl]trimethylammonium bromide (PBTMA) in AOT and pyrenebutyric acid (PBA) in BHDC. The fluorescent quantum yields and lifetimes of the exciplexes were determined as a function of the surfactant concentration and the water content of the microemulsion. The fluorescence of the MP-DMA exciplex is quenched with respect to pure benzene by both reversed micellar systems. When the water content of the solution increases, the fluorescence quantum yield decreases in AOT, while it increases in BHDC. For the probes bound to the micelle's interface the emission maximum is red-shifted with respect to benzene. In BHDC solutions the fluorescence of the exciplexes is drastically quenched by the surfactant. Triplet quantum yields and radical ion quantum yields were determined by laser flash photolysis. In AOT solution radical ions are only present when the exciplex is formed in the interface. In BHDC solutions radical ions are observed in all cases. The yield increases with the surfactant concentration and the water content. The results are interpreted as a consequence of the formation of clusters under percolation conditions which may favor the charge separation in the geminate radical ion pair.

Introduction

Reversed micelles in organic solvents are droplets of water surrounded by a layer of an amphiphilic compound. In these systems there are three different compartments in which small probe molecules can be solubilized: the internal water pool, the interface formed by a monolayer of the surfactant molecules, and the external organic phase.¹⁻³ Exciplex formation was proposed as a good method to obtain information on the average localization site of probes in reversed micelles.⁴ Exciplexes have been studied extensively in homogeneous solutions. They are characterized by large dipole moments, and their fluorescence properties are strongly dependent on the environment polarity.

A 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^{5,6} and radical ions in polar solvents^{7,8} and organized systems.⁹⁻¹¹

The behavior of the pyrene-DMA exciplex in reversed micelles has received attention recently. It was reported

that the quenching of the exciplex by the water pools of the reversed micelles is very efficient and the rate constants are comparable to those calculated by simple diffusion theory.¹² In laser flash photolysis experiments, only the triplet state of pyrene was observed and a quenching model was proposed in which an exciplex formed in the homogeneous phase penetrates the interface. While at the interface, it can deactivate, diffuse back to the oil phase, or penetrate the water pool where it can dissociate into radical ion pairs.¹³

In a previous paper¹⁴ we reported the behavior of exciplexes formed between pyrene derivatives with DMA in sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reversed micelles. The organic phase was an aliphatic hydrocarbon (*n*-heptane or *n*-decane). It was found that when the pyrenyl group forms part of a detergent-like probe, bound to the interface of AOT micelles, the fluorescent properties of the exciplexes are dependent on the length of the aliphatic chain of the probe.¹⁴ In these systems, the fluorescent emission maxima of the exciplexes shift to the red and their fluorescence quantum yields and fluorescence decay times decrease with the water content in the reversed micelles.

In the present paper we report the fluorescent properties of several exciplexes made of a pyrene derivative and DMA in AOT/benzene and benzylhexadecyldimethylammonium chloride (BHDC)/benzene solutions. We selected the systems under study in such a way that a cationic pyrene derivative and an anionic one were bound to an anionic and cationic interface, respectively. A neutral probe was studied in both interfaces. The fluorescent properties of the exciplexes depend on the amount of water dissolved in the microemulsion, the polar head, and the concen-

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tration of the surfactant molecules. In BHDC/benzene solutions, measurable amounts of radical ions are observed and an attempt to correlate the quantum yield of radical ions with the electrical percolation of the solutions is made.

Experimental Section

Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) was purchased from Sigma. It was dried under vacuum and used without further purification. Benzylhexadecyldimethylammonium chloride (BHDC) was also from Sigma; it was recrystallized several times from ethyl acetate and dried under vacuum. (4-(1-Pyrenyl)butyl)-trimethylammonium bromide (PBTMA) and pyrenebutyric acid (PBA) were products from Molecular Probes and were employed as received. 1-Methylpyrene (MP) was a gift of Professor E. Lissi. *N,N*-Dimethylaniline (DMA), Merck, was distilled under vacuum immediately before use. Benzene, Sintorgan HPLC grade, was dried and distilled before use.

All experiments were done under controlled temperature at 30 °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. In these experimental conditions the average number of probes per micelle is less than one.

In all cases the water pool was prepared with 0.001 M Tris buffer solutions adjusted to pH 8 in order to assure that PBA is in its anionic form and therefore anchored to the interface. The fluorescence spectra and the fluorescence quantum yields of PBA were the same in BHDC solutions when the water pool was prepared with water at pH 8 or 11 ([KOH] = 0.001 M).

Fluorescence spectra were obtained in an Aminco Bowman spectrofluorometer. The fluorescence quantum yields of the exciplexes were measured in solutions containing 5×10^{-6} M probe and 0.06 M DMA. At this quencher concentration the fluorescence intensity of the pyrene derivative was reduced to less than 10% of the value without DMA. The fluorescence quantum yields were measured relative to quinine bisulfate in 0.1 N sulfuric acid as standard.

The fluorescence lifetime equipment consisted of a nitrogen laser (ClOp, 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 to analyze the decay curves just over a two-decade range. The estimated error in the decay times was $\pm 3\%$ or ± 0.5 ns, whichever is greater.

The setup for transient absorption experiments consisted of 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 analyzing beam from a Xenon arc lamp. The detection system comprises a $f/4$ monochromator and a red extended photomultiplier (Hamamatsu R666 or RCA 4840). Transient signals were acquired in a way similar to that of the fluorescence decays.

The quantum yield determinations of the pyrene triplet state and pyrene radical anion were done at 422 and 495 nm, respectively. The extinction coefficients¹⁵ of the triplet-triplet absorption of pyrene derivatives in benzene were taken as $20\,900\text{ M}^{-1}\text{ cm}^{-1}$, and that of the pyrene anion radical¹⁶ was taken as $90\,000\text{ M}^{-1}\text{ cm}^{-1}$. The triplet absorption at 470 nm of a solution of zinc tetraphenylporphyrin in benzene was used as a standard for quantum yield determinations.¹⁷ The concentrations of the solutions containing the pyrene derivative were around 5×10^{-6} M and were matched in absorbance at 337 nm, the wavelength of the exciting laser. In all cases the DMA concentration was large enough to reduce the fluorescence of the probe to less than 90%.

The conductivity measurements were performed at 30 °C with a Beckmann RC-18A conductivity bridge.

Table I. Fluorescence Parameters of the MP-DMA Exciplex and Triplet State and Radical Ion Quantum Yields in AOT/Benzene and BHDC/Benzene Solutions at 30 °C

solvent	ϕ_T	λ_{max} (nm)	τ (ns)	ϕ_T	ϕ_{ion}	ϕ_{back}
0.05 M AOT						
$R = 0$	0.188	475	112	0.29		0.40
$R = 4$	0.178	475	108	0.30		0.40
$R = 10$	0.168	475	101	0.30		0.41
0.2 M AOT						
$R = 0$	0.178	475	108	0.27		0.43
$R = 4$	0.154	475	105	0.28		0.45
$R = 10$	0.131	475	93	0.26		0.49
0.05 M BHDC						
$R = 0$	0.042	475	26	0.26	0.020	0.56
$R = 10$	0.143	475	55	0.23	0.018	0.49
$R = 20$	0.163	475	74	0.25	0.025	0.44
0.2 M BHDC						
$R = 0$	0.023	475	13	0.25	0.024	0.58
$R = 10$	0.047	475	23	0.24	0.045	0.55
$R = 20$	0.061	475	31	0.22	0.066	0.53
benzene	0.266	475	112	0.44		0.17

Results

I. Exciplex Formation in Reversed Micelles. a. Probe in the Organic Phase. When AOT is dissolved in benzene, it forms microemulsions which are optically transparent and stable upon the addition of water until a molar water to AOT ratio (R) of 12. Beyond this value the solution is optically opaque. In the same solvent BHDC forms stable reversed micelles up to $R = 25$. MP was used as a exciplex-forming probe in the organic phase. The fluorescence spectrum and fluorescence decay times of MP in the reversed micelle solutions are the same as those obtained in benzene.

The addition of DMA to an AOT or BHDC solution of MP results in the quenching of its fluorescence. The fluorescence quenching rate constants for the MP probe were practically the same at all the detergent concentrations and R values studied. They were also similar to the fluorescence quenching rate constant of MP by DMA in benzene ($4 \times 10^9\text{ M}^{-1}\text{ s}^{-1}$). This quenching is accompanied by the characteristic exciplex emission. The fluorescence excitation spectra observed at the monomer or exciplex emission maxima were the same. Table I gives the fluorescence decay times, the emission maximum, and the fluorescence quantum yield of the exciplexes at two detergent concentrations and different R values.

From Table I it can be observed that, in AOT solutions, the position of the emission maximum of the exciplex MP-DMA does not change with the water content or with the AOT concentration. This maximum is coincident with that obtained in benzene solutions. In AOT solutions the exciplex fluoresces with a lower quantum yield and a shorter lifetime than in pure benzene. The quenching is apparent even at very low R values. In Figure 1 the quenching of the exciplex by AOT is shown at several R values. It can be seen that it increases with the water content of the system. From the values in Table I, it is clear that the emission quantum yields are quenched to a larger extent than the lifetimes.

In Table I the experimental results obtained in 0.05 and 0.2 M solutions of BHDC in benzene are also presented. The data in this table show that, at $R = 0$, the fluorescence quantum yields of the exciplex are 1 order of magnitude lower than those in the AOT/benzene system. The position of the emission maximum is independent of R at all the concentrations of BHDC studied. The fluorescence quantum yield and fluorescence decay time behavior with water content is opposite that in AOT. They increase with R at all concentrations of BHDC. On the other hand

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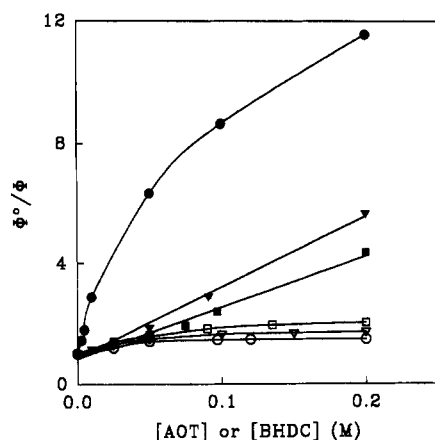


Figure 1. Stern-Volmer plots for the quenching of MP-DMA exciplexes by AOT and BHDC in benzene solutions at 30 °C: (○) AOT, $R = 0$; (▽) AOT, $R = 4$; (□) AOT, $R = 10$; (●) BHDC, $R = 0$; (▼) BHDC, $R = 10$; (■) BHDC, $R = 20$.

when R is constant, they decrease as the surfactant concentration increases. In Figure 1 the Stern-Volmer (SV) plot for the quenching of the MP-DMA exciplex by BHDC is also shown. From Figure 1, the large efficiency of BHDC relative to AOT in the quenching of the MP-DMA exciplex at $R = 0$ can be seen. It can also be observed that at $R = 10$ and 20 the SV plots are linear.

b. Probe Bound to the Micellar Interface. The positive probe PBTMA was used in conjunction with AOT/benzene solution where it can be considered to be totally bound to the micellar interface. It is almost insoluble in pure benzene. Upon the addition of AOT it becomes strongly fluorescent, and its fluorescence decay time could be fitted within the experimental error, by a single exponential at all the AOT concentrations and R values studied. Its absorption and emission spectra were similar to those observed in solutions of AOT in other solvents.¹⁴ This means that the excited probe molecules constitute a single and homogeneous population bound to the negative interface.¹⁸

The fluorescence of PBTMA is also strongly quenched by DMA in AOT solutions. At the same time the typical exciplex emission is observed. The data presented in Table II show that the fluorescence quantum yields and fluorescence decay times of the exciplex PBTMA-DMA are strongly dependent on the water content of the microemulsion and they decrease as R increases. Here again, as in the case of the MP-DMA exciplex, the lifetimes do not decrease to the same extent as the exciplex emission quantum yields. The fluorescence emission maximum of the exciplex is also dependent on the water content of the microemulsion. It shifts to the red when R increases, Figure 2, but its position is independent of the AOT concentration. The emission maxima are shifted by a few nanometers to longer wavelengths in respect to the position of the same exciplex in AOT/heptane solutions.¹⁴

The negative probe PBA can be considered totally bound to the BHDC micellar interface when the water pool is kept at basic pH. Under these conditions the probe shows a single exponential decay. DMA quenches the PBA fluorescence in these solutions with simultaneous appearance of exciplex emission. At 0.05 M the emission quantum yield is very low. The maximum wavelength is shifted to the red by only 3 nm with respect to pure benzene, but the lifetime and quantum yields are reduced to a greater extent. As before the reduction in the lifetime is less than the

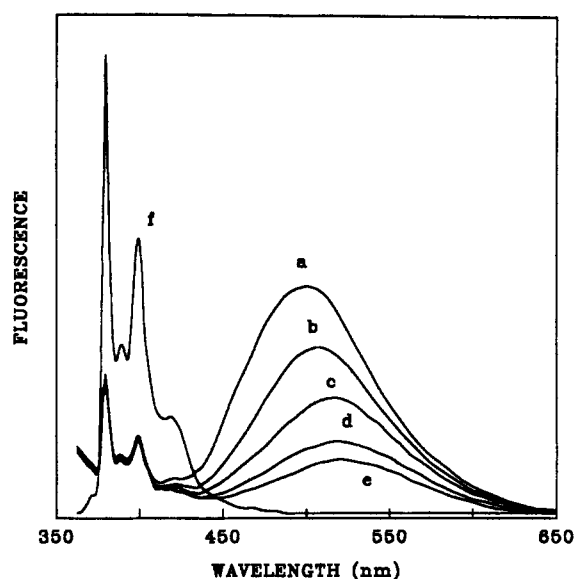


Figure 2. Fluorescence emission spectra of the PBTMA-DMA exciplex in 0.2 M AOT/benzene solutions as a function of R : [PBTMA] = 5×10^{-6} M; [DMA] = 0.06 M; (a) $R = 0$; (b) $R = 2$; (c) $R = 4$; (d) $R = 8$; (e) $R = 10$; (f) emission spectrum of PBTMA in benzene/0.2 M AOT (vertical scale $\times 15$).

Table II. Fluorescence Parameters of the PBTMA-DMA and PBA-DMA Exciplexes and Triplet State and Radical Ion Quantum Yields in AOT/Benzene and BHDC/Benzene Solutions at 30 °C

solvent	ϕ_f	λ_{\max} (nm)	τ (ns)	ϕ_T	ϕ_{ion}	ϕ_{back}
PBTMA-DMA						
0.05 M AOT						
$R = 0$	0.128	500	110	0.50		0.26
$R = 4$	0.080	516	82	0.45	0.005	0.35
$R = 10$	0.039	526	54	0.36	0.006	0.48
0.2 M AOT						
$R = 0$	0.121	500	107	0.46		0.30
$R = 4$	0.062	516	77	0.41	0.006	0.42
$R = 10$	0.031	526	48	0.31	0.006	0.54
PBA-DMA						
0.05 M BHDC						
$R = 0$	0.022	535	19	0.29	0.025	0.54
$R = 10$	0.024	480	44	0.25	0.029	0.58
$R = 20$	0.026	480	63	0.26	0.039	0.55
0.2 M BHDC						
$R = 0$	0.018	535	14	0.25	0.020	0.59
$R = 10$	not detected			0.22	0.042	0.62
$R = 20$	not detected			0.21	0.064	0.60
benzene	0.260	477	106	0.43		0.19

static quenching of the emission. In the absence of water, $R = 0$, the exciplex emission is at 535 nm with a lifetime very much lower than that in the micellar solutions. This probably corresponds to an exciplex formed in PBA-BHDC aggregates. In Figure 3 it is shown that it changes to the "normal" micellar exciplex when water is added and the reversed micelles are formed. At 0.2 M the exciplex emission can only be observed in the absence of added water.

II. Laser Flash Photolysis Experiments. For all the system under study, the emission quantum yields and lifetimes of the exciplexes were lower in reversed micellar solutions than in benzene. In order to get information about the fate of the exciplexes, laser flash photolysis experiments were conducted on these systems. The transient species observed at 1 μ s after the pulse were the triplet state of the pyrene derivative and the radical ions, except for the system MP-DMA in AOT where the latter were unobserved. Under these conditions the transient spectra ascribed to radical ions can be considered due to

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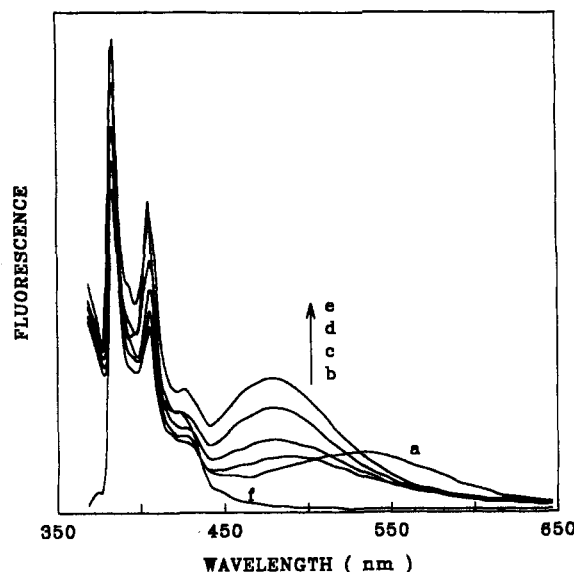


Figure 3. Fluorescence emission spectra of the PBA-DMA exciplex in 0.05 M BHDC/benzene solutions as a function of R : [PBA] = 5×10^{-6} M; [DMA] = 0.06 M; (a) $R = 0$; (b) $R = 2.5$; (c) $R = 5$; (d) $R = 10$; (e) $R = 20$; (f) emission spectrum of PBA in 0.05 M BHDC/benzene (vertical scale $\times 30$).

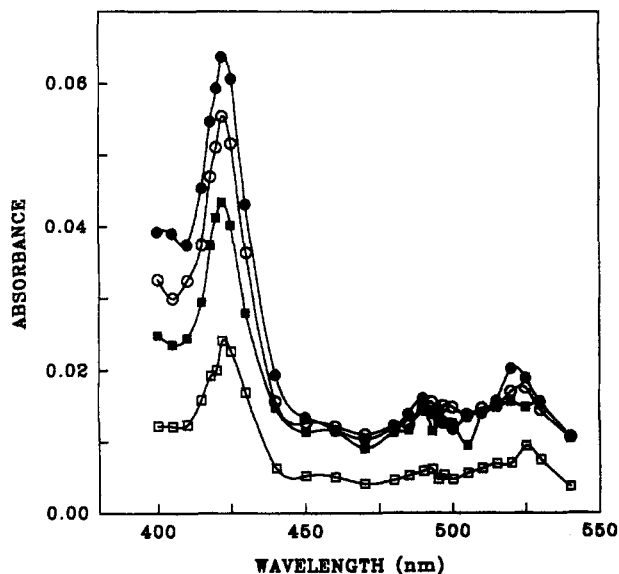


Figure 4. Transient absorption spectra of PBTMA in the presence of DMA in benzene/0.2 M AOT solutions as a function of R : (●) $R = 0$; (○) $R = 4$; (■) $R = 10$; (□) in the absence of DMA at $R = 10$; [PBTMA] = 5×10^{-6} M and [DMA] = 0.06 M.

free ions. The quantum yields of triplet and radical ions for all the systems are collected in Tables I and II.

a. Triplet-State Yields. In AOT/benzene solutions laser flash photolysis experiments were performed for MP and PBTMA in the presence and absence of DMA at several R values. In all cases the spectrum of the pyrene triplet state, which presents a maximum at 422 nm, was observed. Figure 4 shows the spectra of the system PBTMA-DMA taken at 1 μ s after the laser flash. Similar ones were obtained for MP-DMA.

The triplet quantum yield of MP in solutions free of DMA is $\phi_T = 0.21$, independent of R . When DMA is added to the solutions, so that more than 90% of the singlet state of MP is quenched, the characteristic enhancement of the intersystem crossing by charge-transfer interaction¹⁹ was observed, Table I. The triplet quantum yields in micellar

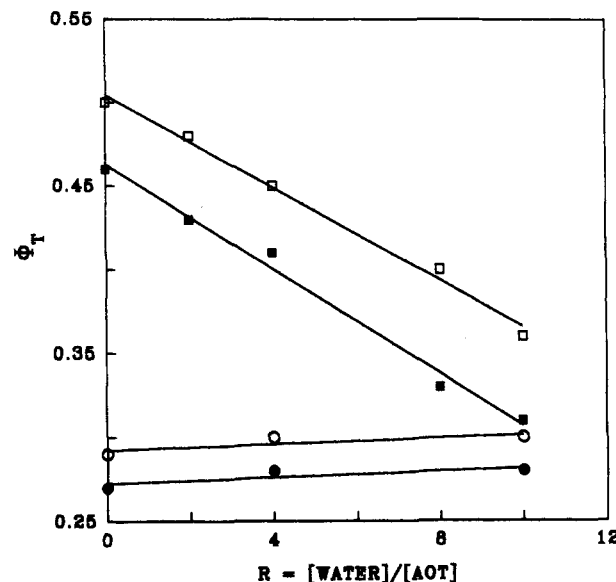


Figure 5. Triplet yields of the MP-DMA and PBTMA-DMA systems in AOT/benzene solutions as a function of R : (○) MP-DMA, 0.05 M AOT; (●) MP-DMA, 0.2 M AOT; (□) PBTMA-DMA, 0.05 M AOT; (■) PBTMA-DMA, 0.2 M AOT.

solutions are plotted against R in Figure 5. It can be seen that for this probe they are approximately independent of R .

For the probe PBTMA in AOT/benzene, the triplet quantum yield in solutions free of DMA is $\phi_T = 0.17$ and it is independent of R . The addition of DMA to the solutions results in a large quantum yield of pyrene triplets at $R = 0$. For this probe the triplet yield decreases with R and with AOT concentration as can be seen in Figure 5.

In BHDC solutions the triplet quantum yield of MP in the presence and the absence of DMA is very similar to that obtained in AOT solutions. It is almost independent of R and the BHDC concentration, Table I. The transient absorption spectrum of PBA in the absence and presence of DMA is shown in Figure 6. For this probe the triplet quantum yield is also almost independent of R and BHDC concentration, Table II.

b. Radical Ion Yields. In AOT solution radical ions were not observed on our time scale for MP-DMA and observed only in minute amounts for PBTMA-DMA, Table II and Figure 4. As opposed to AOT, in BHDC solutions the pyrene radical anion absorption at 495 nm is clearly observed for both probes. Quantum yields ϕ_{ion} are collected in Tables I and II. For MP-DMA in 0.05 M solutions the pyrene radical anion quantum yield is almost independent of R . However, for 0.2 M solutions ϕ_{ion} abruptly increases with R as can be seen in Figure 7a. For PBA-DMA in BHDC the results are not much different from those obtained for the MP-DMA system, Table II. In Figure 6 the transient absorption spectra of the PBA-DMA system at different R in 0.2 M BHDC solutions can be observed. The intensity of the absorption band centered at 495 nm increases markedly with R . The quantum yield of the radical anion also depends on the concentration of BHDC.

III. Electrical Conductivity of the Reversed Micelle Solutions. It is known that in BHDC/benzene/water solutions over a certain volume fraction of the dispersed phase (water plus BHDC) the conductivity of

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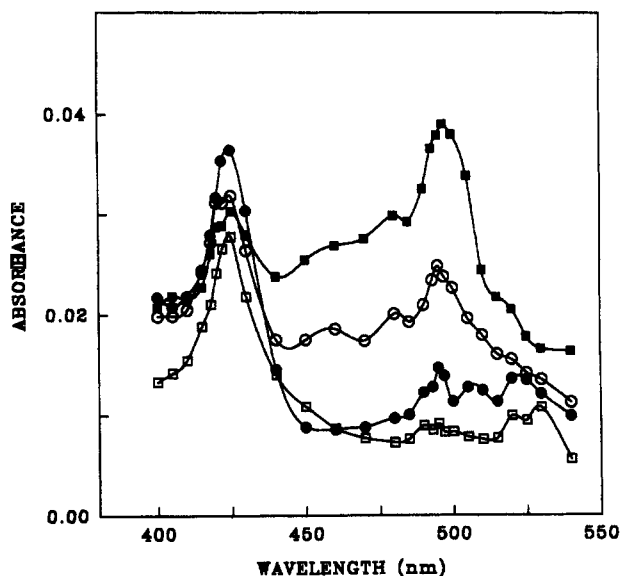


Figure 6. Transient absorption spectra of 5×10^{-5} M PBA in the presence of 0.06 M DMA in 0.2 M BHDC/benzene solutions as a function of R : (●) $R = 0$; (○) $R = 10$; (■) $R = 20$; (□) in the absence of DMA at $R = 20$.

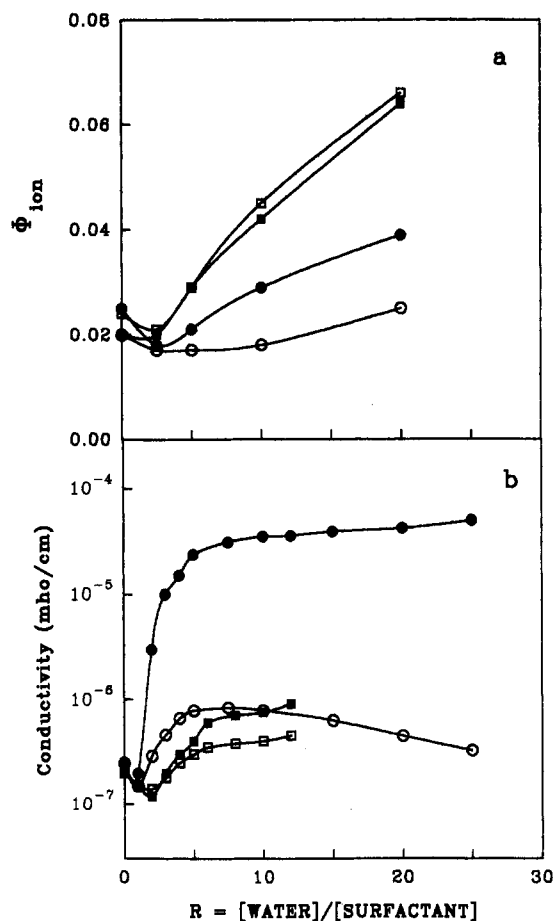


Figure 7. (a) Radical anion yields of the MP-DMA and PBA-DMA systems in BHDC/benzene solutions as a function of R : (○) MP-DMA, 0.05 M BHDC; (□) MP-DMA, 0.2 M BHDC; (●) PBA-DMA, 0.05 M BHDC; (■) PBA-DMA, 0.2 M BHDC. (b) Electrical conductivity of BHDC/benzene and AOT/benzene solutions as a function of R : (○) 0.05 M BHDC; (●) 0.2 M BHDC; (□) 0.05 M AOT; (■) 0.2 M AOT.

the solutions begins to increase sharply, yielding what is known as an electrical percolation transition.^{20,21} In order to investigate if this transition is related to the fate of the exciplex and the quantum yield of radical ion formation,

conductivity measurements were performed on the same solutions employed for the quantum yield determinations.

Figure 7b shows the variations of electrical conductivity (K) as a function of R for the 0.05 and 0.2 M solutions of AOT and BHDC. The electrical conductivities of the AOT solutions and the 0.05 M BHDC solution remain almost constant over the range of R studied. However, a large rise of the electrical conductivity is observed in the 0.2 M BHDC solution when R increases. The last result is characteristic of microemulsions that suffer a percolative electrical conduction transition. In Figure 7 it can be seen that for 0.2 M BHDC solutions the region of increasing radical ion yield coincides with that of increasing conductivity.

Discussion

I. Probe in the Organic Phase. a. MP-DMA Exciplex. It was observed that in AOT/heptane solutions the probe MP and the quencher DMA are partitioned between the interface and the solvent bulk.¹⁴ In AOT/benzene solutions, however, the fluorescence emission spectrum of both MP and DMA does not change with the water content of the microemulsion and it is coincident with the spectrum observed in benzene. This result together with the observed similar fluorescence quenching rate constants of MP by DMA in AOT and benzene solutions suggests that the exciplex is mainly formed in the organic phase at all the R values. The quenching of the exciplex emission observed in the microemulsions can be explained by a mechanism similar to that proposed by Kikuchi and Thomas for the quenching of the pyrene-DMA exciplex in AOT/heptane reversed micelles.¹² From the values of emission quantum yields and lifetimes for two AOT concentrations in Table I it can be seen that there is an important contribution from a static quenching mechanism. The static contribution to the quenching can be ascribed to a global increase of the solution polarity when water is added to the system. The dynamic measurements afford a bimolecular rate constant for quenching at $R = 10$ of $(8.5 \pm 0.5) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ based on AOT concentration. To our knowledge, the aggregation number of AOT reversed micelles in benzene is not known. If an aggregation number similar to that in heptane is assumed, i.e., 108 for $R = 10$,²² a micelle concentration based rate constant of $9.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ results. This is more than 1 order of magnitude lower than the value of $2.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ given by Kikuchi and Thomas¹² in AOT/heptane for the same R . If the supposition about the aggregation number is not totally wrong, this result indicates that the AOT/benzene interface presents a higher barrier for the interaction of the polar interior of the micelles with the exciplex than that of AOT/heptane. These observations are also in agreement with the lack of radical ion formation in the exciplex quenching.

In BHDC/benzene the MP-DMA exciplex presents a behavior diverse from that in AOT. For the same surfactant concentration the emission quantum yields are lower in BHDC. The results in Table I show that, within the experimental error, in this case the decrease in emission quantum yields is coincident with the decrease in lifetime with increasing detergent concentration. The most striking difference is the trend in the fluorescence quantum yields with changing water content. While in AOT solutions, the quantum yields decrease with R for the

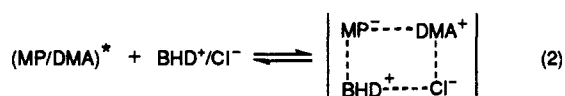
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exciplexes studied; in BHDC solutions they increase. As can be seen in Figure 1 BHDC at $R = 0$ is very much more effective than AOT in the quenching of the exciplex. This large quenching may be explained on the basis of the model proposed for the quenching of several exciplexes by organic and inorganic salts.²³⁻²⁶ In aprotic solvents of low dielectric constant, bulky ions form contact ion pairs. At low water content the detergent will be mainly in the form of ion pairs. These ion pairs are believed to be the quenching species. Probably an ion pair associates with the exciplex to form an intermediate complex with the characteristics of a quadrupole, which favors nonradiative transitions to the ground state. Ammonium salts are more efficient as quenchers than alkaline salts,²⁶ and this can explain the low fluorescence quenching of the exciplexes by AOT.

The quenching mechanism by BHDC can be represented by eqs 1-3, where BHD⁺ stands for the benzylhexadecyldimethylammonium cation. This quenching mechanism



can explain the observed increase in emission quantum yields and lifetimes with R . When water is added, the reversed micelles begin to form and less detergent ionic pairs are left free for quenching the exciplex. The fact that the emission maximum of the exciplex in BHDC solutions is at the same wavelength as in benzene also indicates that the exciplex is formed in the organic phase. When all the polar groups of BHDC are hydrated and the reversed micelles are formed with their water pools, there is still a BHDC concentration quenching effect. This quenching can be explained with the model proposed by Kikuchi and Thomas.¹² In this case the quenching is due to the reversed micelle as a whole, and not to the ion pairs. The bimolecular rate constant at 30 °C and $R = 20$ is $1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ based on BHDC concentration which corresponds to $8.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ per micelle concentration when an aggregation number of 700 is used.²⁷ This number is to be compared with $4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for pyrene-DMA at 25 °C and the same R .¹² The same agreement is found at other R values.

The laser flash photolysis experiments indicate that in AOT the only transient species formed in the quenching of MP by DMA is the excited triplet of the probe. No free radical ions are observed. The triplet yield is higher than in benzene in the absence of DMA, but lower than that for the same quenching fraction by DMA in the pure organic solvent. From Table I it can be observed that the triplet quantum yield is practically independent of the AOT concentration and water content of the solutions. The net effect of the organized system is an increase in the rate of return to the ground state, probably by geminate electron back-transfer of the exciplex. On the other hand, in BHDC while triplets are formed with similar quantum yields, free radical ions are produced. Their yields, although small, show a trend with R and surfactant

concentration which is related to the exciplex decay. The quantum yield for electron back-transfer is given in the last column of Table I. It was calculated from the following equations:

$$\phi_{\text{back}} = f_{\text{Q}} - \phi_{\text{f}} - \phi_{\text{ion}} - [\phi_{\text{T}} - (1 - f_{\text{Q}}) \times \phi_{\text{T}}^{\circ}]$$

$$f_{\text{Q}} = \frac{K_{\text{SV}}[\text{Q}]}{1 + K_{\text{SV}}[\text{Q}]}$$

where ϕ_{f} , ϕ_{T} , and ϕ_{ion} are the quantum yields of exciplex fluorescence, the triplet state of the probe, and the free radical ions, respectively. ϕ_{T}° is the triplet yield in the absence of DMA, and f_{Q} is the fraction of MP excited singlets quenched by DMA.

In 0.05 M BHDC solutions the quantum yield of the ions only shows a small increment at $R = 20$, Figure 7a. This may be the result of the increasing polarity of the system. In 0.2 M BHDC solutions the quantum yield of ions increases with the water content. At this concentration the exciplex fluorescence yield and lifetime are also greatly reduced. This can be understood by comparison with the conductivity results. It is currently admitted that a microemulsion, with a low fraction of the dispersed phase, can be described by spherical water droplets surrounded by a surfactant layer and dispersed in the organic solvent. When the fraction of the dispersed phase increases and it is near the onset of percolation, the aggregation of droplets is observed²⁰ in BHDC/benzene/water microemulsions. Above the percolation threshold, an increasing number of droplets are associated in clusters (including infinite clusters) and these droplets are constantly forming and breaking apart.²¹ Since the exciplex MP-DMA is produced principally in the organic phase, the special structure of the solution under percolating conditions must be responsible for the increased yield of ions. The large rate constant for exchange of material between droplets and the formation of clusters may favor the charge separation in the geminate radical ion pair.

II. Probe Bound to the Interface. a. PBTMA-DMA Exciplex in AOT/Benzene. The probe PBTMA is bound to the AOT interface; therefore, the PBTMA-DMA exciplex is formed in the micellar interface. The red shift of the emission maximum of the exciplex and the reduction in its fluorescence quantum yield and decay times on the addition of water to the AOT solution are characteristic of the behavior of exciplexes when the solvent polarity increases. The observed spectral changes when R increases are similar to those observed for the PBTMA-DMA exciplex in AOT/alkane solutions.¹⁴ However, the emission maxima are shifted to the red by a few nanometers with respect to the values in this solvent. The results suggest that the exciplex is sensing a slightly larger dielectric constant in AOT/benzene than in AOT/heptane solutions at the same values of R .

The laser flash photolysis experiments indicate that the quenching of the PBTMA singlet state by DMA leads to the excited triplet as the principal decay route of the exciplex. Although in small yields, radical ions are also produced. This indicates that the micropolarity of the interface, where the exciplex is formed, is large enough to allow the charge separation. The reduction in the fluorescence quantum yield and fluorescence decay time of the exciplex where R increases is also indicative of that possibility. The triplet yield decreases with increasing R , and at the same time radical ions are observed and the back-recombination yield increases. This can be explained by the following reaction scheme, proposed by Saito and Kikuchi:¹³

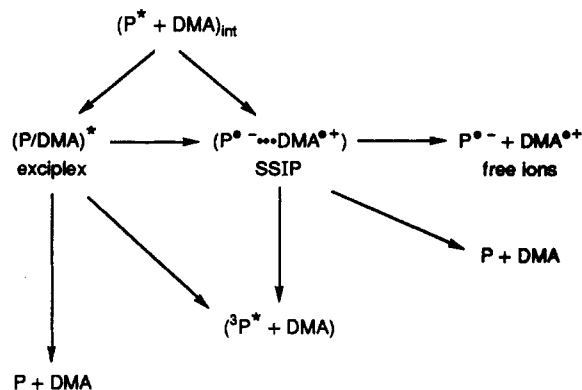
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In the scheme two possible intermediates to the triplet state are proposed, the solvent-separated ion pair (SSIP) and the exciplex. The existence of this differentiated structure has been demonstrated in homogeneous electron-transfer systems. If the triplet originates mainly in the contact ion pair (exciplex) but not in the SSIP, this could explain the observed trend in the yields in Table II. When R increases, the micropolarity of the interface increases,¹⁴ and the formation of the solvent-separated ion pair (SSIP) is favored. Therefore, a decrease in the triplet quantum yield with R should be observed.

b. PBA-DMA Exciplex in BHDC/Benzene. The quenching of the PBA-DMA exciplex by BHDC at $R = 0$ can be explained in a way similar to that used above for the MP-DMA exciplex. However, the interaction of PBA with BHDC is stronger, as is reflected by the large red shift of the exciplex fluorescence band at $R = 0$. Also the larger initial slopes in the quenching of the exciplex, Figure 1, mainly due to static quenching, reflect this strong interaction.

The addition of water to a 0.05 M BHDC solution produces a blue shift in the exciplex emission and an increase in the fluorescence decay time of the exciplex. When the reversed micelles are formed, the exciplex emission is shifted to the blue with respect to the interfacial

exciplex in AOT solutions. This is an indication that it is formed in a less polar region of the interface.

In BHDC solutions even at $R = 0$ the formation of the transient pyrene radical anion is observed. This may be the result of the large interaction between the exciplex and the polar headgroups of BHDC through the quadrupolar interaction responsible for the fluorescence quenching. It was previously observed that in homogeneous solutions the addition of tetrabutylammonium perchlorate to a solution containing an exciplex produces higher quantum yields of radical ions.²⁵ Counterion exchange makes it possible to separate the radical ion pair initially formed, avoiding electron back-transfer to the ground state. As can be seen in Figure 7a the increase of the quantum yield with R is more pronounced for 0.2 M BHDC. This can be explained by assuming that the increase in the radical ion yield is the sum of two factors, an intrinsic one due to the association with the polar heads of BHDC and another that reflects the increasing polarity of the system. This last effect is more important in the 0.2 M BHDC solutions and as discussed before is related to the percolation of the solutions.

The triplet quantum yield for this system is slightly dependent on the surfactant concentration. As can be observed from the values in Table II, the decrease in ϕ_T on going from 0.05 to 0.2 M is approximately compensated by the increase in ϕ_{ion} . This can be explained by the same reaction scheme as before, by a competition of the two decay routes of the SSIP; in this case the formation of the triplet state from the SSIP must be taking place in order to explain the observed changes in quantum yields with concentration, and also it can explain the independence with R of the triplet yield at a given BHDC concentration.

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