Fluorescence Probes in Reversed Micelles. Luminescence Intensities, Lifetimes, Quenching, Energy Transfer, and Depolarization of Pyrene Derivatives in Cyclohexane in the Presence of Dodecylammonium Propionate Aggregates

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Abstract: Pyrene (PY), pyrenebutyric acid (PBA), pyrenesulfonic acid (PSA), and 8-hydroxy-1,3,6-pyrenetrisulfonic acid (pyranine) have been used as fluorescence probes in 0.08 M dodecylammonium propionate (DAP) in cyclohexane in the presence of different amounts of cosolubilized water. Solubilities have indicated that pyranine is located in the surfactant solubilized water pools and that both PSA and PBA bind strongly to DAP. Rate constants for quenching the fluorescence of PY by CCl_4 in cyclohexane are unaffected by the presence of DAP. This probe is located, therefore, in the bulk solvent and it does not interact with DAP. Fluorescence energy of PBA is efficiently quenched by CCl_4 in the presence of the DAP aggregates but not by KBr. PBA is likely to be lined up along the alkyl chains of the DAP aggregates such that its carboxylate group is close to the micellar interior but its aromatic moiety is near the bulk hydrocarbon solvent. Conversely, PSA, having no alkyl chain, is pulled in closer to the micellar core, and its excitation energy is quenched both by KBr and by CCl_4. Assuming spherical geometry, average sizes of aggregates have been calculated for 0.08 M DAP in cyclohexane as a function of cosolubilized water concentration. Increasing the amount of water results in a rapid increase of the average aggregation number from a small value of 7 to 115. At a stoichiometric concentration of less than 0.37 M, all of the water molecules are tied up in hydrating the surfactant headgroups. As the water concentration increases, the increase of the size of DAP aggregates is paralleled by an increase in the number of free water molecules entrapped in the reversed micelles. Fluorescence polarization data of pyranine support these calculations. An efficient energy transfer has been observed from DAP solubilized PBA in cyclohexane to terbium chloride, located in the surfactant solubilized water pools. The mechanism of this process is discussed in terms of excitation of PBA, followed by intersystem crossing to the triplet domain which is sufficiently long lived to allow its diffusion to the acceptor molecules. The role of surfactant aggregates is to compartmentalize no more than one molecule of donor per aggregate, thereby preventing triplet-triplet annihilation.

Introduction

Surfactant aggregates in nonpolar solvents, termed reversed micelles, are attracting increasing attention.[3-10] They are capable of solubilizing copious quantities of water and polar molecules. Rates of many reactions are dramatically enhanced in the environment of reversed micelles. Even more significant is the observed high degree of specificity for these rate enhancements.[11] Favorable substrate partitioning, orientation, concerted proton transfer (if applicable), and the unique properties of the media have been proposed to be responsible for the effects on reaction rates. Indeed, depending on the amount of water added, i.e., on the size of the water pool, the microscopic polarity of the cosolubilized substrate could be varied over a considerable range.[12]

Our understanding of the factors which determine the extent of catalysis in reversed micelles is sadly lacking. The type and concentration of the surfactant, the mode of its aggregation, the polarity of the organic solvent, the size of the water pools, and the nature of the substrate are the many parameters which need to be considered in the rationalization of reaction kinetics in reversed micellar systems.[3] In the absence of additives, association of alkylammonium carboxylates in organic solvents is of the monomer $\rightleftharpoons$ dimer $\rightleftharpoons$ trimer $\rightleftharpoons n$-mer type.[13-15] In this system, the average aggregation number depends on the stoichiometric surfactant concentration and it is in the order of 3-10.[16,17] Conversely, in the presence of water and bulky substances, surfactant aggregates in nonpolar solvents may contain several hundred monomers.[12,18] The nature of aggregation in these multicomponent systems has not been explored. Our primary concern is, however, the elucidation of substrate-surfactant interactions in organic solvents in the presence of relatively small amounts of solubilized water pools. Using ^1H NMR spectroscopic techniques, the predominant solubilization sites of 2,3,4,6-tetramethyl-D-glucose,[19] dimethyl sulfoxide,[20,21] methanol,[20,21] pyrazole,[20,21] 2-pyridone,[20,21] and tetrabutylammonium perchlorate[20,21] were established to be in close proximity to the polar surfactant headgroups in organic solvents. NMR experiments rely, however, on rather high substrate concentrations—a condition which differs substantially from the kinetic investigations. Fluorescence techniques allow the utilization of substrates in micromolar concentration and they provide information on their microenvironments in terms of viscosity, rigidity, and proximity.[22-27] Fluorescence probes have been advantageously utilized in the reversed micellar Aerosol-OT in heptane.[28,29] We have examined the interaction of pyrene, pyrenesulfonic acid, pyrenebutyric acid, and 8-hydroxy-1,3,6-pyrenetrisulfonic acid (pyranine) with dodecylammonium propionate aggregates in cyclohexane in the presence of different amounts of cosolubilized water. Different hydrophobicities of these pyrene derivatives will likely orient them to different positions in the reversed micelles. The predominant localization of these probes can be inferred from their fluorescence spectra, lifetimes, and quenching while fluorescence depolarization provides information on their microscopic viscosities.

Investigations of photophysical processes in micellar environments are not only inherently interesting or are relevant to the understanding of photobiology but they do have practical implications. Micelles organize donor and acceptor molecules in a recognizable manner.[30,31] Thus, for example, naphthalene solubilized in anionic micellar sodium dodecyl sulfate efficiently transfers energy to terbium chloride.[32] In the absence of micelles, there is no observable energy transfer. Sodium dodecyl sulfate micelles have been shown to compartmentalize no more than one donor molecule into each micellar interior and to concentrate a large number of terbium chloride mole-

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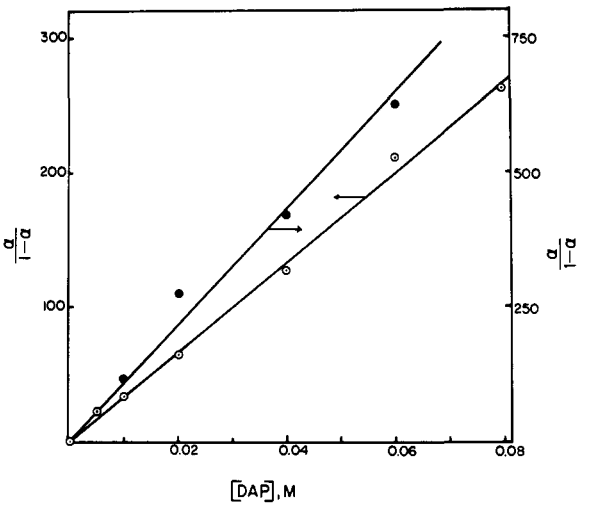

Figure 1. Plot of the solubility data according to eq 1 for PBA (⊙) and PSA (●) in DAP in cyclohexane in the presence of 2.78×10^{-2} and 5.56×10^{-2} M water, respectively.

cules at their charged surface. Triplet-triplet annihilation, an important photophysical process in water, is obviated by the micelles.[32] Favorable organization of donor and acceptor molecules in micellar compartments may well lead to the design of economically feasible solar energy conversion systems.[33,34] Surfactant aggregates in nonpolar solvents represent an alternative, possibly a superior, system for the investigation of compartmentalized energy transfer. The present work also represents our initial efforts in obtaining understanding of energy transfer processes in reversed micelles.

Experimental Section

Pyrenebutyric acid (PBA, Pfaltz and Bauer) was recrystallized twice from ethanol-water (70:30 v/v) and dried over P_2O_5. Pyrenesulfonic acid (PSA), 8-hydroxy-1,3,6-pyrenetrisulfonic acid, pyranine, and pyrene (PY, Eastman) were used as received. Dodecylammonium propionate (DAP) was prepared by the method of Kitahara[35] and was twice recrystallized from *n*-hexane. Terbium chloride ($TbCl_3 \cdot 6H_2O$, Alfa Ventron) was used as received. The good agreement between the observed and reported[36] excitation and emission spectra verified the purity of this compound. Deionized water was distilled from an all-glass equipment prior to use. Spectral grade cyclohexane (Mallinckrodt) was dried and stored over Lynde type 4-A molecular sieves. Its water content was maintained to be less than 10 ppm. All the other chemicals were of the best available reagent grade and were used without further purification.

Absorption spectra were taken on a Cary 118C UV-visible recording spectrophotometer equipped with a thermostated cell compartment. Steady state luminescence spectra and fluorescence polarization spectra were obtained on a SPEX Fluorolog spectrofluorometer in the E/R mode. Generally, 2.5-mm slits with 10-nm band path were used. Fluorescence lifetimes were determined by means of a modified Ortec 9200 single photon counting nanosecond time resolved fluorescence spectrometer,[37,38] with the output displayed on a multichannel analyzer. Excitation wavelengths were selected by the use of appropriate filters (Ditric Optics, Inc.) having a 15-nm half-height bandwidth. Fluorescence lifetimes were calculated either graphically[39] or on an IBM 360 computer using the method of moments program.[40] Since fluorescence lifetimes observed in the present work far exceeded the half-width of the lamp pulse (ca. 2 ns) computer calculated lifetimes agreed well with those determined graphically. All spectral work was carried out at 25.0 ± 0.1 °C. Luminescence spectra and lifetimes for all solutions were determined on degassed samples. Degassing was carried out on a high-vacuum line using repeated freeze-pump-thaw cycles. The water content of samples was determined by gas-liquid partition chromatography as described previously.[41] Ground-state dissociation constants of PBA and pyranine in water were determined by potentiometric titrations using standardized 0.01 N HCl and measuring the pH on a Radiometer pHM-26 instrument to be 6.6 and 7.2.

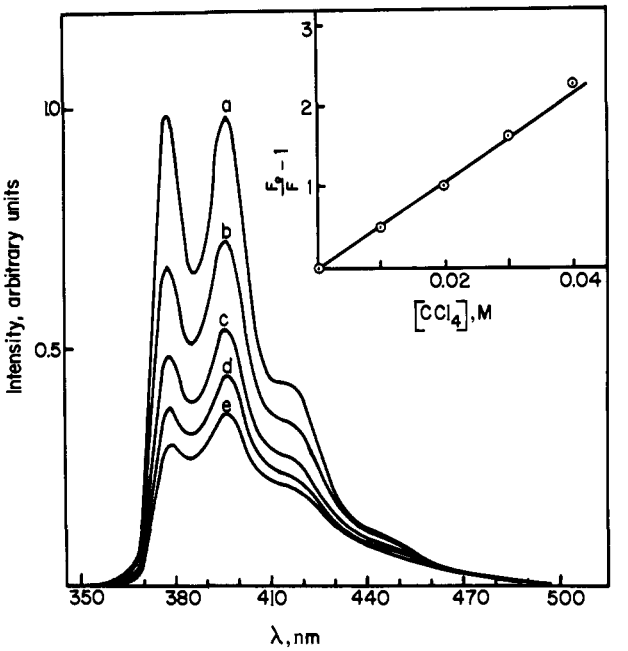

Figure 2. Fluorescence emission spectra of 5.0×10^{-5} M PBA in 0.08 M DAP in cyclohexane in the presence of 0 (a), 0.01 (b), 0.02 (c), 0.03 (d), 0.04 M (e) CCl_4. Insert shows the Stern-Volmer plot of the data according to eq 2.

Results

Pyrenebutyric Acid (PBA). Pyrenebutyric acid is not very soluble in cyclohexane. Its solubility was determined to be 1.3×10^{-4} M spectrophotometrically. Addition of increasing amounts of DAP results in the solubilization of substantial amounts of PBA. In 0.08 M DAP in cyclohexane PBA is some 260-fold more soluble than in the absence of the surfactant. Solubility data of PBA in cyclohexane in the presence of different amounts of DAP were utilized for the calculation of the binding constant, K, for the association of PBA with DAP from[42]

$$\frac{\alpha}{1-\alpha} = \frac{K}{\bar{N}} C_D \qquad (1)$$

where α is the relative solubility of PBA in the presence and in the absence of DAP, C_D is the stoichiometric surfactant concentration, and $\bar{N}$ is the average aggregation number. Plotting the left-hand side of eq 1 against the concentration of DAP resulted in a good straight line (Figure 1) from which $K/\bar{N}$ was calculated to be 3.3×10^3 M^{-1}.

Absorption, excitation, and emission spectra of PBA in cyclohexane were found to be identical with those reported previously.[43,44] There were excitation maxima at 326 and 343 nm. Upon excitation at 343 nm, the emission maxima of PBA were found to occur at 370, 387, and with a shoulder at 403 nm. These spectroscopic parameters remained independent of the PBA concentration in the $(3.3\text{-}67) \times 10^{-3}$ M range in the presence of 0.08 M DAP and were unaffected by the addition of DAP.

Carbon tetrachloride quenched the fluorescence of PBA both in the absence and in the presence of DAP. Figure 2 illustrates the emission spectra of 5.0×10^{-2} M PBA in 0.08 M DAP in cyclohexane in the presence of increasing amounts of CCl_4. Quenching of the excited state of PBA was quantitatively treated in terms of the Stern-Volmer equation:

$$\frac{F^0}{F} - 1 = k_q \tau_0 [Q] \qquad (2)$$

where F and F^0 are fluorescence intensities of the probe in the presence and in the absence of the quencher, k_q is the

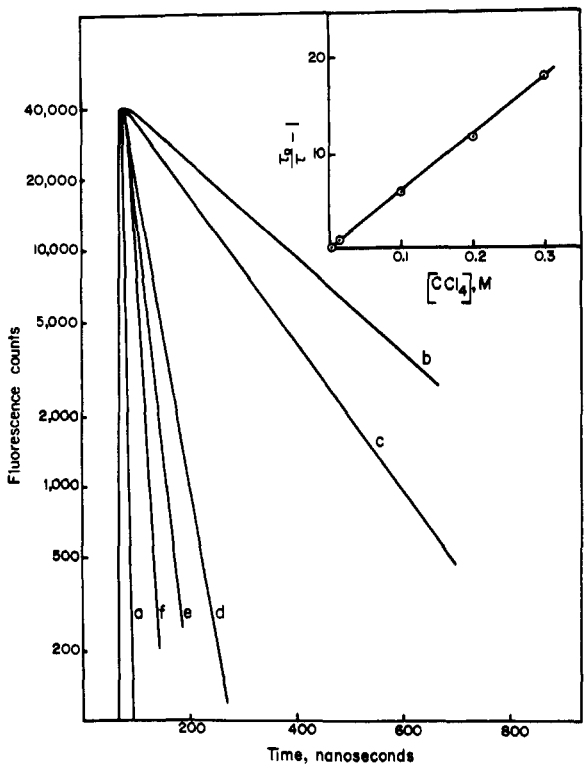

Figure 3. Decays of the nanosecond light pulser (a) and of 5.0×10^{-5} M PBA in 0.08 M DAP in cyclohexane in the presence of 0 (b), 0.010 (c), 0.10 (d), 0.20 (e), and 0.30 M (f) CCl_4. Insert shows the treatment of the data according to eq 3.

quenching rate constant, [Q] is the concentration of the quencher, and τ_0 is the fluorescence lifetime of the probe in the absence of the quencher. The insert in Figure 2 shows a plot of the data according to eq 2.

Fluorescence lifetimes of PBA in neat water and in neat cyclohexane were determined to be 130 and 220 ns, respectively (Table I). These lifetimes are in good agreement with the reported values.[45,46] Addition of 0.08 M DAP did not alter the fluorescence lifetime of PBA in cyclohexane. Significantly, however, the presence of cosolubilized water markedly shortened the fluorescence lifetimes of PBA in DAP reversed micelles in cyclohexane. The lifetime decreased from 220 to 204 ns subsequent to the addition of as little as 5.56×10^{-3} M water. Increasing the concentration of cosolubilized water up to 2.96×10^{-1} M resulted in further decrease of the fluorescence lifetime down to 169 ns. This value did not alter, however, upon increasing further the size of the DAP solubilized water pool (Table I). Decreasing the fluorescence lifetime with increasing water concentration was not a consequence of the alteration of the microscopic pH of PBA in the reversed micelles since changes in hydrogen ion concentration did not affect the fluorescence decay of PBA in water (Table I).

Addition of quenchers decreased the fluorescence lifetimes. Thus the fluorescence lifetime of PBA in 0.08 M DAP in cyclohexane in the presence of 1.23×10^{-2} M water, 217 ns, decreases to 12 ns in the presence of 0.30 M carbon tetrachloride. Figure 3 illustrates typical decays of the intensities of the nanosecond light pulser and those of the fluorescence of PBA in 0.08 M DAP in cyclohexane in the absence and presence of carbon tetrachloride. Decay time data were also used for the calculation of quenching rate constants, k_q, from the equation

$$\frac{\tau^0}{\tau} - 1 = k_q \tau_0 [Q] \qquad (3)$$

where τ^0 and τ are the fluorescence lifetimes of the probe in the absence and in the presence of the quencher. Plots of the left-hand side of eq 3 against the quencher concentration generally resulted in good straight lines. The insert on Figure 3 illustrates such a typical plot. Rate constants for quenching of PBA fluorescence by CCl_4, KBr, and $TbCl_3$ in different solvents are collected in Table II. It is interesting to observe that neither KBr nor $TbCl_3$ quenches the fluorescence of PBA in cyclohexane in the presence of DAP surfactant aggregates (Tables I and II). Conversely, quenching by CCl_4 is somewhat more efficient in the presence of reversed micelles than in their absence.

Terbium chloride is readily taken up into the DAP solubilized water pools in cyclohexane. Cosolubilization of (0.67–13.3) $\times 10^{-5}$ M PBA resulted in substantial enhancement of the intensities of the $TbCl_3$ emission bands. The enhanced intensity of Tb(III) luminescence was found to be dependent on both the $TbCl_3$ and PBA concentration (Table III). In-

Table I. Fluorescence Lifetimes of PBA

Condition[a]	Lifetime, ns[b]
In water, unbuffered	130 (97)[c]
In water, pH 2.2[d]	146
In water, pH 4.3[d]	125
In water, pH 5.5[d]	129
In water, pH 7.0[d]	124
In water, pH 10.0[d]	123
In water, pH 11.5[d]	127
In cyclohexane	222 (24)[c]
In cyclohexane + 0.08 M DAP	217
In cyclohexane + 0.08 M DAP + 5.56×10^{-3} M H_2O	204
In cyclohexane + 0.08 M DAP + 1.04×10^{-2} M H_2O	203
In cyclohexane + 0.08 M DAP + 1.85×10^{-2} M H_2O	193
In cyclohexane + 0.08 M DAP + 5.56×10^{-2} M H_2O	190
In cyclohexane + 0.08 M DAP + 2.96×10^{-1} M H_2O	169
In cyclohexane + 0.08 M DAP + 4.81×10^{-1} M H_2O	169
In cyclohexane + 0.08 M DAP + 0.41×10^{-1} M H_2O	185
In cyclohexane + 0.08 M DAP + 3.3 M KBr in 0.41 M H_2O[e,f]	185
In cyclohexane + 0.08 M DAP + 1.0×10^{-3} M $TbCl_3$ in 1.85×10^{-2} M H_2O	192

[a] [PBA] = $(2.5\text{–}5.0) \times 10^{-5}$ M. All solutions were degassed by repeated freeze-pump-thaw cycles on a high vacuum line, unless stated otherwise. Excitation wavelength 315 nm, emission wavelength 370 or 398 nm. [b] These lifetimes are accurate within 2%. [c] Air-saturated solutions. [d] Adjusted by NaOH or HCl. [e] Containing 1.0×10^{-2} M NaOH. [f] Prepared by injecting 3.3 M KBr in 1.0×10^{-2} M NaOH to give appropriate water concentration.

Table II. Rate Constants, k_q Values, for Quenching PBA Fluorescence

Quencher[a]	Medium	k_q, M^{-1} s^{-1}[b]
KBr	H_2O	9.0×10^6
	Cyclohexane + 0.08 M DAP + 1.23×10^{-2} M H_2O	6×10^5[c]
CCl_4	Cyclohexane	9.4×10^7
	Cyclohexane + 0.08 M DAP + 1.23×10^{-2} M H_2O	2.6×10^8 (2.5×10^8)[d]
$TbCl_3$	H_2O	3.5×10^7
	Cyclohexane + 0.08 M DAP + 1.23×10^{-2} M H_2O	6×10^5[c]

[a] Concentration of CCl_4 is expressed as the stoichiometric solute added to the organic solvent. Concentrations of the inorganic quenchers refer to the amounts present in the surfactant solubilized water pools. [b] Determined from fluorescence lifetimes according to eq 3, unless stated otherwise. [c] Upper limit. [d] Determined from steady state fluorescence according to eq 2.

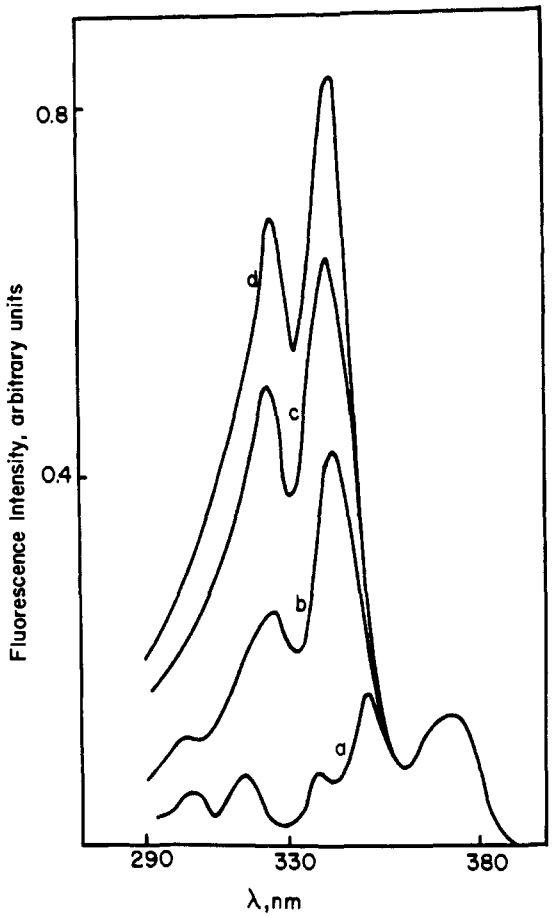

Figure 4. Excitation spectra of 3.3×10^{-3} M $TbCl_3$ in 0.08 M DAP in cyclohexane in the presence of 0.092 M H_2O and 0 (a), 6.67×10^{-6} (b), are 1.33×10^{-5} (c), 3.33×10^{-5} M (d) PBA. Emission wavelength 546 nm.

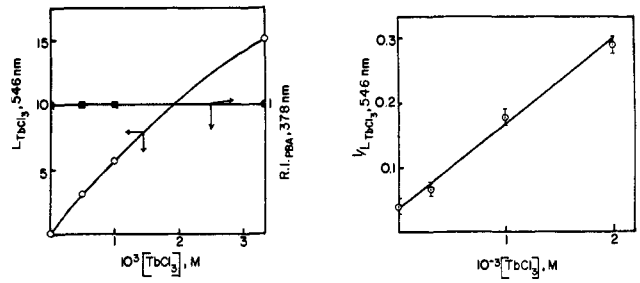

Figure 5. Left-hand side: plots of luminescence intensities of $TbCl_3$ at 546 nm (⊙) and fluorescence intensities of PBA at 378 nm (■) against $TbCl_3$ concentrations in 0.08 M DAP in cyclohexane containing 6.0×10^{-5} M PBA and 9.25×10^{-2} M H_2O. Right-hand side: plot of $TbCl_3$ luminescence vs. $TbCl_3$ concentration according to eq 19. In 0.08 M DAP in cyclohexane containing 6.0×10^{-5} M PBA and 9.25×10^{-2} M H_2O.

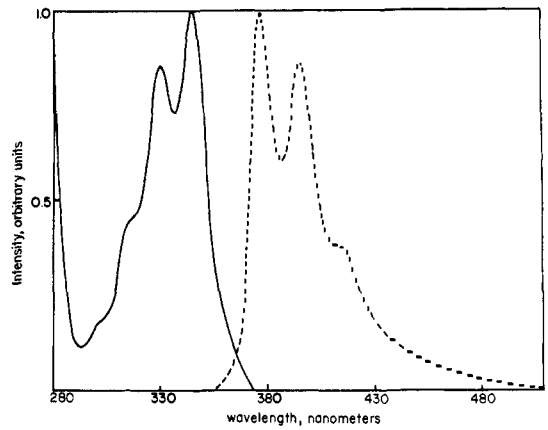

Figure 6. Excitation (solid line) and emission (broken line) spectra of 2.0×10^{-6} M PSA in 0.08 M DAP in cyclohexane in the presence of 5.56×10^{-2} M H_2O. Excitation is observed at 380 nm; emission is observed at 346 nm.

Table III. Relative Intensity of $TbCl_3$ Luminescence as a Function of PBA and $TbCl_3$ Concentrations[a]

10^5[PBA], M	10^3[$TbCl_3$], M[b]	RI[c]
0	3.33	1.00
0.67	3.38	5.25
1.33	3.33	8.88
2.00	3.33	10.80
4.67	3.33	17.50
6.00	0.50	4.30
6.00	1.00	7.00
6.00	3.33	18.90
6.68	3.33	19.10
8.00	3.33	17.10
10.00	3.33	14.00
13.30	3.33	9.50

[a] In cyclohexane containing 0.08 M DAP and 9.25×10^{-2} M H_2O. [b] Concentration of $TbCl_3$ expressed as that present in the surfactant solubilized water pool. [c] Excitation wavelength 343 nm; emission wavelength 491 nm.

creasing the PBA concentration in the $(0.67\text{-}6.7) \times 10^{-5}$ M range resulted in a sigmoidal increase of the relative emission intensity of Tb(III) up to a maximum after which there is a decrease. The decrease of fluorescence intensity was dependent on the geometry of the system and on the molar absorptivity of the donor at the excitation wavelength and was, therefore, attributed to inner filter effects.[47,48] Excitation spectra of the same solutions, taken using 546 nm as the emission wavelength, showed greatly enhanced intensities upon the addition of PBA (Figure 4). Since PBA does not emit at the wavelength at which the excitation spectrum was analyzed (546 nm) these results imply that energy is transferred from PBA to Tb(III) via an excited state. At a constant PBA concentration increasing concentrations of $TbCl_3$ resulted in an increase of Tb(III) emission intensity (left-hand side of Figure 5). Fluorescence intensities (Figure 5) and lifetimes of PBA (Table I) remained unaltered, however, in the presence of $TbCl_3$. These results are compatible with the noninvolvement of PBA singlet excited states in the energy transfer and exclude the possibility of the reabsorption of the PBA fluorescence by $TbCl_3$. There is no energy transfer under our experimental conditions in water in the absence of a surfactant.

Pyrenesulfonic Acid (PSA). Pyrenesulfonic acid is also solubilized by DAP in cyclohexane. Increasing concentrations of DAP increased the solubility of this probe. Relative solubilities, treated according to eq 1, gave a good straight line (Figure 1) from which $K/N = 1.0 \times 10^4$ was calculated for the association of PSA with DAP in cyclohexane in the presence of 5.56×10^{-2} M cosolubilized water.

Figure 6 shows the excitation spectra of 2.0×10^{-6} M PSA in 0.08 M DAP in cyclohexane. The observed excitation (330 and 347 nm) and emission (374 and 394 nm) maxima are in good agreement with those reported previously.[46] Table IV gives the fluorescence lifetimes of PSA in different solvent systems. The observed lifetime in water agrees well with that determined previously.[46] Addition of water to DAP solubilized PSA in cyclohexane results in only a minor decrease of the fluorescence lifetimes. However, both KBr and CCl_4 quench the PSA fluorescence. Dynamic quenching of PSA fluorescence obeyed eq 3 (Figure 7). Table V summarizes the quenching rate constants. The rate constant for KBr quenching

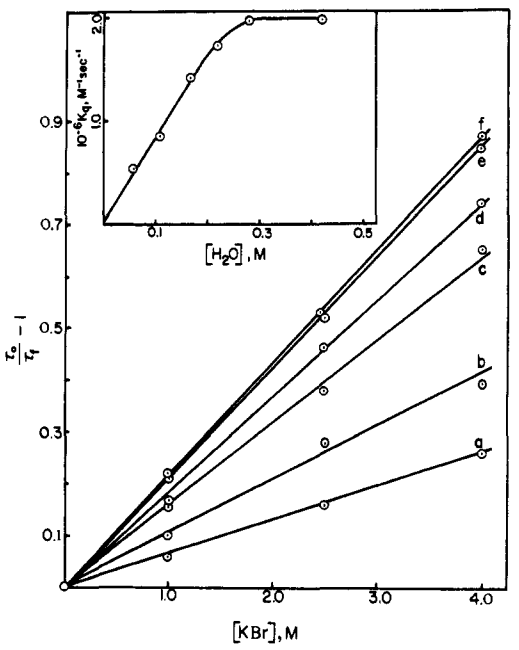

Figure 7. Treatment of the quenching of fluorescence decay according to eq 3 of 1.25×10^{-4} M PSA by KBr in 0.08 M DAP in cyclohexane in the presence of 5.56×10^{-2} (a), 1.11×10^{-1} (b), 1.67×10^{-1} (c), 2.22×10^{-1} (d), 2.80×10^{-1} (e), and 4.2×10^{-1} M (f) water. The insert shows a plot of the quenching rate constant vs. cosolubilized water concentration.

Table IV. Fluorescence Lifetimes of PSA

Condition[a]	Lifetime, ns[b]
In water, unbuffered	63 (62)[c]
In cyclohexane + 0.08 M DAP	119
In cyclohexane + 0.08 M DAP + 5.0×10^{-3} M H_2O	120
In cyclohexane + 0.08 M DAP + 2.9×10^{-1} M H_2O	109
In cyclohexane + 0.08 M DAP + 1.11×10^{-1} M H_2O[d]	115
In cyclohexane + 0.08 M DAP + 1.67×10^{-1} M H_2O[d]	113
In cyclohexane + 0.08 M DAP + 2.22×10^{-1} M H_2O[d]	111
In cyclohexane + 0.08 M DAP + 2.78×10^{-1} M H_2O[d]	109
In cyclohexane + 0.08 M DAP + 3.33×10^{-3} M $TbCl_3$ in 9.25×10^{-2} M H_2O	111

[a] [PSA] = $(1-2) \times 10^{-4}$ M. All solutions were degassed by repeated freeze–pump–thaw cycles on a high vacuum line. Excitation wavelength 350 nm; emission wavelength 380 nm. [b] These lifetimes are accurate within 2%. [c] Reference 46. [d] Containing 1.0×10^{-2} M NaOH.

of PSA fluorescence is 16-fold smaller in the reversed micellar cavity than that in bulk water. Increasing the size of the DAP solubilized water pool results in a sigmoidal increase of k_q values (Table V and insert in Figure 7). CCl_4 is a more efficient quencher and the quenching rate does not depend on the size of the water pool.

PSA transfers its excited state energy to terbium chloride in cyclohexane in the presence of 0.08 M DAP. The relative luminescence intensity of $TbCl_3$, observed at 546 nm, increases sigmoidally in the range of $(2-10) \times 10^{-6}$ M PSA, and it reaches a plateau at 1.2×10^{-5} M PSA. At this point, the relative luminescence intensity is approximately three times greater in the presence of PSA than that in its absence. This energy transfer is considerably less efficient than that observed for PBA. Once again, no energy transfer is observed in water in the absence of a surfactant.

8-Hydroxy-1,3,6-pyrenetrisulfonic Acid (Pyranine). Pyranine is completely insoluble in cyclohexane. Using the most sensitive range of 100 counts on the SPEX Fluorolog, no emission was detected in the supernatant of saturated solutions

Table V. Rate Constants, k_q Values, for Quenching PSA Fluorescence

Quencher[a]	Medium	k_q, M^{-1} s^{-1}
KBr	H_2O	8.2×10^7
	Cyclohexane + 0.08 M DAP + 5.56×10^{-2} M H_2O	0.55×10^6
	Cyclohexane + 0.08 M DAP + 1.1×10^{-1} M H_2O	0.86×10^6
	Cyclohexane + 0.08 M DAP + 1.7×10^{-1} M H_2O	1.42×10^6
	Cyclohexane + 0.08 M DAP + 2.2×10^{-1} M H_2O	1.72×10^6
	Cyclohexane + 0.08 M DAP + 2.8×10^{-1} M H_2O	1.98×10^6
	Cyclohexane + 0.08 M DAP + 4.4×10^{-1} M H_2O	1.97×10^6
CCl_4	Cyclohexane	2.89×10^8
	Cyclohexane + 0.08 M DAP	1.67×10^7
	Cyclohexane + 0.08 M DAP + 0.30 M H_2O	1.09×10^7
	Cyclohexane + 0.08 M DAP + 0.30 M H_2O (containing 1.0×10^{-2} M NaOH)	1.25×10^7
$TbCl_3$	H_2O	2.75×10^7
	Cyclohexane + 0.08 M DAP	3.0×10^5[b]

[a] Concentration of CCl_4 is expressed as the stoichiometric solute added to the organic solvent. Concentrations of the inorganic quenchers refer to the amounts present in the surfactant solubilized water pools. [b] Upper limit.

of pyranine in cyclohexane. Determination of a concentration of 10^{-8} M pyranine is well within the means of our detection and is considered the upper limit of solubility. In 0.08 M DAP in cyclohexane, containing 2.78×10^{-2} M H_2O, 2.3×10^{-4} M pyranine was found to be soluble. In water, pyranine is considerably more soluble, of course. A saturated solution (in 55.5 M water) was found to contain 0.51 M pyranine. Assuming that all the water molecules are at the interiors of the surfactant aggregates, the solubility of pyranine in 2.78×10^{-2} M water pools approaches closely that of a saturated solution in bulk water. This observation implies the sequestering of pyranine well within the DAP entrapped water pools in cyclohexane.

The excitation (maxima at 252, 296, 375–385, 410 nm) and emission (maximum at 513 nm) spectra in water and in 0.08 M DAP in cyclohexane correspond closely to those reported previously.[49]

The fluorescence lifetime of pyranine is fairly short. It was found to be 5.5 ± 1.0 ns in degassed solutions of water and in 0.08 M DAP in cyclohexane. Furthermore, addition of up to 4.0 M KBr did not quench the decay of pyranine fluorescence.

Depolarization of pyranine fluorescence is very sensitive, however, to the microenvironment of this probe. The intensity of emission was measured at perpendicular ($I_{\perp\parallel}$, $I_{\parallel\perp}$) and parallel ($I_{\perp\perp}$, $I_{\parallel\parallel}$) positions of the polarizers at 510 nm. The subscripts denote the orientation of the electric vector of the light which passes the excitation (first symbol) and the emission (second symbol). The symbols $\perp$ and $\parallel$ mean horizontal and vertical orientation. The degree of polarization is given by the equation[50]

$$P = \frac{I_{\parallel\parallel} - I_{\parallel\perp}(I_{\perp\parallel}/I_{\perp\perp})}{I_{\parallel\parallel} + I_{\parallel\perp}(I_{\perp\parallel}/I_{\perp\perp})} \quad (4)$$

and eq 5[51] relates the polarization to the viscosity of the me-

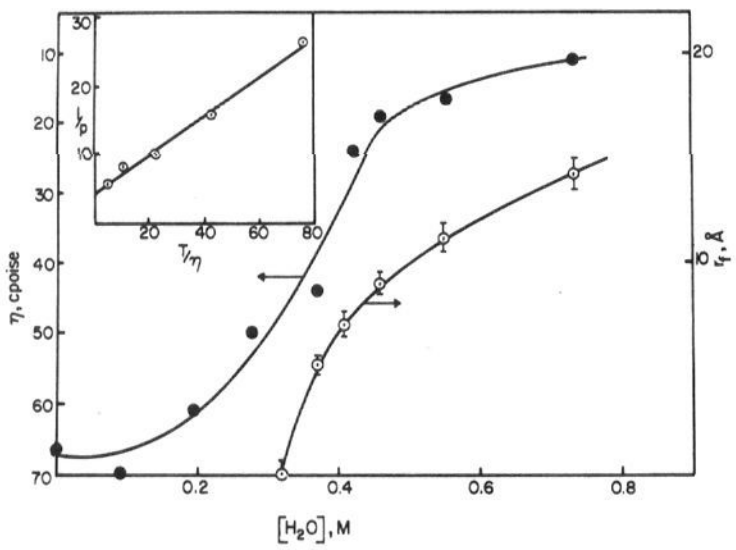

Figure 8. A plot of microviscosities of 0.08 M DAP in cyclohexane as a function of cosolubilized water concentration (left-hand side scale) and a plot of calculated radius of surfactant entrapped free water pools at different stoichiometric water concentrations (right-hand side scale). The insert shows the calibration plot of pyranine polarization in glycerol–water mixtures.

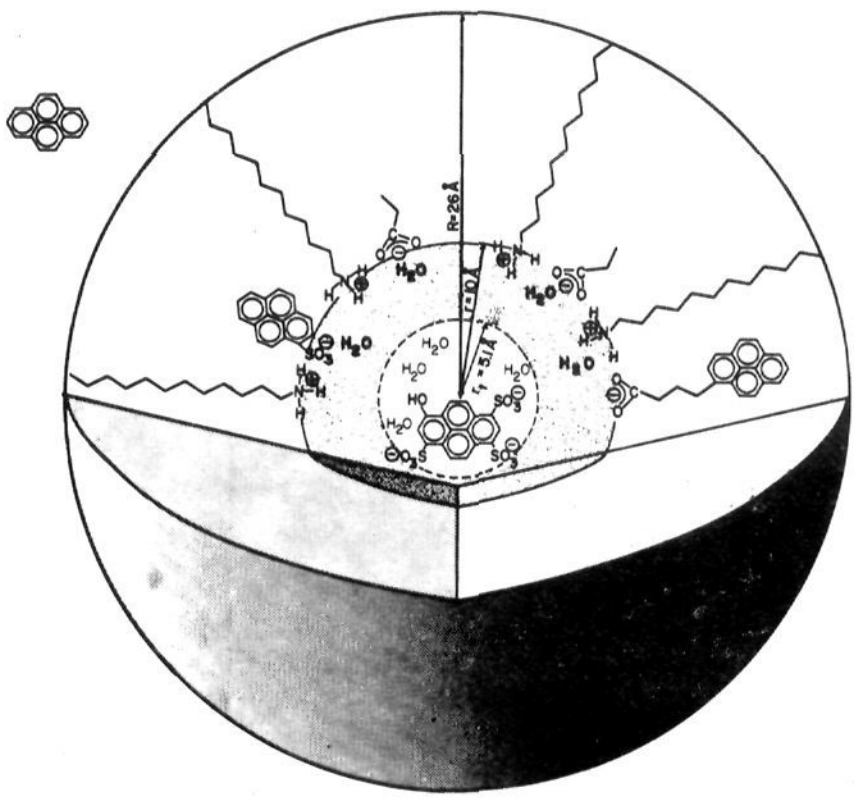

Figure 9. An oversimplified representation of 0.08 M DAP aggregate in cyclohexane in the presence of 0.370 M cosolubilized water. The estimated average aggregation number is 30. The radius of the aggregate, R, is 26 Å; that of the water pool, r, is 10 Å, and that of the free water pool, r_f, is 5.1 Å. The proposed interaction sites of pyrene (PY), pyrenebutyric acid (PBA), pyrenesulfonic acid (PSA), and pyranine are illustrated.

dium (η) in which the probe is dispersed:

$$\frac{\frac{1}{P}-\frac{1}{3}}{\frac{1}{P_0}-\frac{1}{3}} = 1 + \frac{KT\tau}{\eta v_0} \qquad (5)$$

where P_0 is the degree of polarization measured in an extremely viscous solvent, τ is the average lifetime of the molecule in the excited state, v_0 is its effective volume, T is the absolute temperature, and K is the Boltzmann constant. P values in 0.08 M DAP in cyclohexane, at different temperatures and in the presence of different amounts of cosolubilized water, were converted to viscosities by calibration using glycerol–water mixtures of known viscosities. From the linear relationship of the $1/P$ against T/η (insert in Figure 8) the determined P values in reversed micelles were readily converted to viscosities. Addition of 0.40 M water to 0.08 M DAP in cyclohexane is seen to result in a drastic reduction of the microviscosity of pyranine. Further gradual increase of the surfactant solubilized water pool results in a modest decrease of the microviscosity (Figure 8).

Pyrene (PY). Excitation (317, 333, 378 nm) and emission (380 and 401 nm) maxima of PY in 0.08 M DAP in cyclohexane are identical with those reported previously in organic solvents. Quenching rate of the pyrene excited state by CCl_4 was found to be 1.1×10^8 M^{-1} s^{-1} in the presence and 1.3×10^8 M^{-1} s^{-1} in the absence of DAP indicating the lack of interaction of pyrene with the surfactant. No energy transfer from pyrene to $TbCl_3$ was observed in the presence of 0.08 M DAP in cyclohexane.

Under our experimental conditions, no appreciable energy was deposited to the surfactant or to the solvent.

Discussion

Self-association of DAP in cyclohexane has been previously investigated.[15,19,52-54] In the absence of water, the behavior of this surfactant is best described in terms of a sequential indefinite self-association to relatively small aggregates which on the average contain five or more monomers.[19] In the presence of water as cosolubilizate, the type of self-association may be different since the aggregates are increased in size.[3] Experimental and theoretical difficulties precluded, to date, the quantitative determination of the aggregation mechanism of a surfactant in a nonpolar solvent in the presence of varying amounts of water.[14] Using simple geometrical considerations, we have estimated the effects of water on the size of DAP reversed micelles at a given surfactant concentration in cyclohexane. The validity of our estimates is nicely substantiated by fluorescence polarization data.

Average aggregation numbers in 0.08 M DAP in cyclohexane in the presence of different amounts of water have been approximated by calculating the radius of a given reversed micellar interior (r in Figure 9) by two different approaches. The micellar size is taken when the agreement between the two calculations is the best. In both approaches the aggregates as well as the water pools entrapped therein are necessarily assumed to be spherical. In the first approach, the radii of different sized micellar cavities (r_I values in Table VI) are calculated by assuming a surface area of 42 $Å^2$ for the ionic headgroups of one DAP molecule. This assumption is not unreasonable since the limiting surface area at high pressures of all surfactants with a single headgroup per hydrocarbon chain in monolayers is always found to be 21 $Å^2$.[55] In the second approach volumes of surfactant entrapped water pools, hence their radii (r_{II} values in Table VI), are calculated at each cosolubilized water concentration for different aggregation numbers. A value of 1.0 mL/g was taken for the partial specific volume of water by analogy with the available data on Aerosol-OT.[56] The data are collected in Table VI. Best fits, and hence the estimated average aggregation numbers, are given in italics in Table VI.

Several interesting features emerge from these calculations which merit discussion. In the presence of the smallest amounts of cosolubilized water (0.093 M) the calculated radii of the water pool (r_{II}) are smaller at any assumed aggregation number than those estimated from the surface areas of DAP headgroups (r_I). Since an empty space within the micellar cavity is hardly feasible, the most likely explanation is that DAP aggregates which contain little or no water are not spherical. If water is present in excess of 0.185 M in 0.08 M DAP in cyclohexane $r_I < r_{II}$ at low values of $\bar{N}$ but at higher values of $\bar{N}$ $r_{II} < r_I$ (Table VI). The crossover occurs between r_I and r_{II} when an appropriate aggregation number is reached and it is taken to be the best estimate of the size of the reversed micelle at a given cosolubilized water concentration. The estimated average aggregation number is seen to increase with

Table VI. Calculations of Reversed Micellar Parameters in 0.08 M DAP in Cyclohexane in the Presence of Different Amounts of Water and Determined Microviscosities Therein

$[H_2O]$, M[a]	$\bar{N}$[b]	r_I, Å[c]	r_{II}, Å[d]	Number of free H_2O molecules per aggregate	r_f, Å[e]	η,[f] cP	$[H_2O]$, M[a]	$\bar{N}$[b]	r_I, Å[c]	r_{II}, Å[d]	Number of free H_2O molecules per aggregate	r_f, Å[e]	η,[f] cP
0.093	5	4.09	3.50	None		70.2	0.417	5	4.09	5.70			
	6	4.48	3.68					10	5.80	7.19			
	7	4.87	3.87					35	10.80	10.90			
	8	5.17	4.05					*38*	*11.26*	*11.27*	46.08	6.90	23.7
	9	5.48	4.21					40	11.70	11.40			
	10	5.80	4.36					45	12.20	11.90			
	11	6.06	4.50					50	12.90	12.30			
	12	6.33	4.64					60	14.10	13.10			
0.185	5	4.09	4.35	None		59.5	0.463	5	4.09	5.91			
	6	4.48	4.63					10	5.80	7.19			
	7	*4.87*	*4.87*					40	11.70	11.82			
	8	5.17	5.09					*45*	*12.24*	*12.30*	80.43	8.31	19.0
	9	5.48	5.29					48	12.66	12.55			
	10	5.80	5.48					50	12.92	12.75			
	11	6.06	5.66					60	14.15	13.53			
	12	6.33	5.83					65	14.73	13.89			
0.277	5	4.09	4.98				0.556	5	(4.09	6.28			
	10	5.80	6.28					10	5.80	7.91			
	15	7.08	7.18					50	12.92	13.50			
	18	*7.75*	*7.63*	None		49.6		60	14.15	14.40			
	20	8.18	7.91					62	14.39	14.54			
	25	9.14	8.52					*65*	*14.73*	*14.75*	191.8	11.1	16.4
	30	10.00	9.05					100	18.27	17.00			
	35	10.80	9.53					120	20.02	18.12			
0.370	5	4.09	5.48				0.739	5	4.09	6.91			
	10	5.80	6.91					10	5.80	8.70			
	28	9.67	9.75					50	12.92	14.90			
	30	*10.00*	*9.97*	18.75	5.12	44.5		100	17.00	18.60			
	32	10.30	10.20					110	19.20	19.36			
	35	10.80	10.50					*115*	*19.60*	*19.65*	602	16.26	10.3
	70	11.70	11.00					120	20.02	19.90			
	50	12.90	11.80					150	22.38	21.47			

[a] Stoichiometric concentration of added water. [b] Assumed mean aggregation number. [c] Radius of micellar cavities, calculated by assuming (a) surface area of 42 Å^2 for the headgroups of one DAP molecule, (b) spherical water pools, and (c) 1.0 mL/g for the partial specific volume of water. [d] Radius of 0.08 M DAP entrapped water pools, calculated from the known volume of entrapped water assuming (a) spherical water pools and (b) 1.0 mL/g for the partial specific volume of water. [e] Radius of *free* water molecules in micellar cavity. [f] Microviscosity, calculated from pyranine fluorescence data.

increasing water concentration to 115 (Table VI). Lack of water solubility prevented us from examining the behavior of larger water pools in 0.08 M DAP in cyclohexane. The radius of the reversed micelle and that of its water pool (R and r, respectivcly, in Figure 9) increases, in fact, linearly with increasing stoichiometric water concentrations (not shown). A similar situation has been encountered for Aerosol-OT aggregates in dodecane.[56]

The DAP entrapped water pool is not uniform.[3] Addition of small amounts of water to a cyclohexane solution of the surfactant results in the hydration of the amine and the propionate headgroups. Since each DAP molecule was shown to be hydrated by four water molecules in a nonpolar solvent[12] the number of free water molecules per micelle and, hence, the radius of the free water pool, r_f, can be calculated. The data are given in Table VI. All the water molecules are seen to be tied up in hydrating the surfactant headgroups when the concentrations of the stoichiometric water are 0.093, 0.185, and 0.277 M. Free water molecules begin to appear at 0.370 M water concentration. With increasing amounts of cosolubilized water the enlargement of the reversed micelle is paralleled by an increase of free water molecules at the expense of those which hydrate the surfactant headgroups. Changes in the microviscosity of the environment of pyranine in 0.08 M DAP in cyclohexane in the presence of different amounts of cosolubilized water substantiated our treatment. It is seen in Table VI and Figure 8 that when all the available water molecules are tied up hydrating pyranine, the microviscosity is rather high. Anionic pyranine interacts electrostatically with the positive headgroups of DAP with the resultant immobilization of the probe. The appearance of free water molecules in the reversed micellar cavity, at 0.370 M stoichiometric water concentration, corresponds to the change in the rate of microviscosity reduction (Figure 8). At this point pyranine is surrounded by water molecules of hydration. As the concentration of free water in the DAP entrapped pool increases further pyranine is more and more shielded from the charged surfactant headgroups. Consequently, this probe becomes increasingly more mobile and hence it will report lower and lower microviscosities.

Interaction sites of PBA, PSA, and PY with 0.08 M DAP in cyclohexane can be inferred from fluorescence quenching data. It should be emphasized that in all systems, there are considerably fewer than one molecule of probe per aggregate. Pyrene is completely nonpolar and does not partition into the reversed micellar phase. Accordingly, the quenching rate constant of this probe by carbon tetrachloride, a nonpolar quencher, in cyclohexane is the same in the absence and in the presence of DAP. The fluorescence energy of PBA is efficiently quenched by CCl_4, in 0.08 M DAP in cyclohexane (Table II), but it is unaffected by KBr (Table I). These results imply that PBA is lined up along the alkyl chains of the DAP aggregate

such that its carboxylate group is close to the micellar interior but its aromatic moiety is near the bulk hydrocarbon solvent. Furthermore, the solubility of PBA in cyclohexane increased linearly with increasing concentration of the surfactant. At a given PBA concentration, addition of water in the range of (5–500) $\times 10^{-3}$ M does not, however, enhance the solubility. Apparently, the dodecylamine chain of the surfactant is sufficiently thick to prevent energy transfer from the pyrene ring to the ionic quencher, localized in the polar interior of the reversed micelle. Conversely, PSA, having no alkyl chain, is pulled in closer to the micellar core, presumably by dipole-dipole attractions between the sulfonate ion and the surfactant headgroups. The excitation energy of this probe is quenched, therefore, both by KBr and by CCl_4. Figure 9 illustrates the proposed sites of pyrene derivatives in reversed micellar DAP.

There is an apparent increase in k_q values for the quenching of PSA fluorescence by KBr with increasing water concentrations (Table V). This effect can readily be rationalized in terms of the estimated micellar sizes (Table VI). In the presence of small amounts of cosolubilized water there are larger numbers of smaller aggregates. The concentration of the quencher in each aggregate is smaller, therefore. In 0.08 M DAP in cyclohexane in the presence of 5.56×10^{-2} M stoichiometric water which contains 4.0 M KBr less than 25% of the aggregates are occupied by the quencher. The fourfold reduction in k_q value at limited amount of water as compared to larger solubilized water pools is reasonable, therefore. An alternative explanation can be advanced by considering the decrease of viscosity with increasing water concentration (vide supra).

The observed energy transfer from PBA to $TbCl_3$ is explicable in terms of the following photophysical processes for low concentration ($<10^{-5}$ M) of PBA in 0.08 M DAP in degassed solutions of cyclohexane.

$$^1(\text{PBA}) + h\nu \xrightarrow{k_6} {}^1(\text{PBA})^* \quad (6)$$

$$^1(\text{PBA})^* \xrightarrow{k_7} {}^1(\text{PBA}) + h\nu_{\text{PBA}}{}^{\text{F}} \quad (7)$$

$$^1(\text{PBA})^* \xrightarrow{k_8} {}^1(\text{PBA}) \quad (8)$$

$$^1(\text{PBA})^* \xrightarrow{k_9} {}^3(\text{PBA})^* \quad (9)$$

$$^3(\text{PBA})^* \xrightarrow{k_{10}} {}^1(\text{PBA}) + h\nu_{\text{PBA}}{}^{\text{P}} \quad (10)$$

$$^3(\text{PBA})^* \xrightarrow{k_{11}} {}^1(\text{PBA}) \quad (11)$$

$$^3(\text{PBA})^* + {}^3(\text{PBA})^* \xrightarrow{k_{12}} \text{quenching} \quad (12)$$

The singlet excited PBA (formed in eq 6) can return to the ground state by fluorescence emission (eq 7), by radiationless decay (eq 8), or it can intersystem cross to form triplet PBA (eq 9). The PBA triplet, in turn, may decay by phosphorescence emission (eq 10) or by radiationless transition (eq 11) or be returned to the ground state by triplet-triplet annihilation (eq 12).

If terbium chloride is present along with PBA, additional photophysical processes (eq 13–17) need to be considered:

$$(^7\text{F})\text{TB(III)} + h\nu \xrightarrow{k_{13}} (^5\text{D})\text{Tb(III)} \quad (13)$$

$$^1(\text{PBA})^* + (^7\text{F})\text{Tb(III)} \xrightarrow{k_{14}} {}^1(\text{PBA}) + (^5\text{D})\text{Tb(III)} \quad (14)$$

$$^3(\text{PBA})^* + (^7\text{F})\text{Tb(III)} \xrightarrow{k_{15}} {}^1(\text{PBA}) + (^5\text{D})\text{Tb(III)} \quad (15)$$

$$(^5\text{D})\text{Tb(III)} \xrightarrow{k_{16}} (^7\text{F})\text{Tb(III)} + h\nu_{\text{Tb}}{}^{\text{L}} \quad (16)$$

$$(^5\text{D})\text{Tb(III)} \xrightarrow{k_{17}} (^7\text{F})\text{Tb(III)} \quad (17)$$

Terbium chloride may be excited directly (eq 13) or, alternatively, it can act as an energy acceptor from singlet (eq 14) or triplet (eq 15) PBA. The excess energy of the terbium cation may be dissipated by returning to the ground state via luminescence (eq 16), or by radiationless decay (eq 17).

Irradiation at 343 nm and at relatively low intensities ensures energy deposition predominantly in PBA, since the molar absorptivities of PBA are far in excess of $TbCl_3$. Equation 13 therefore can be neglected. The longer lifetime of the PBA triplet as compared to the PBA singlet, lack of quenching of the PBA fluorescence by $TbCl_3$, as well as the spin invariance of the triplet PBA–Tb(III) transfer systems substantiate eq 15 as the main photophysical pathway for energy transfer. The observed luminescence intensity of $TbCl_3$, L_{Tb}, in the presence of 0.08 M DAP in cyclohexane can be described by the equation

$$L_{\text{Tb}} = k_{16}[(^5\text{D})\text{Tb(III)}] = \frac{(k_8 + k_9)k_{16}k_{15}I_{\text{PBA}}[(^7\text{F})\text{Tb(III)}]}{(k_{16} + k_{17})(k_{10} + k_{11} + k_{15}[(^7\text{F})\text{Tb(III)}])(k_7 + k_8 + k_9)} \quad (18)$$

where I_{PBA} is the luminescence intensity of PBA in the absence of $TbCl_3$ and is governed by eq 6. Equation 18 is analogous to that utilized in the triplet-triplet energy transfer mechanism in organic molecules[57] and it can be rearranged to

$$\frac{1}{L_{\text{Tb}}} = \frac{k_{15}\tau_{\text{PBA}}\text{T}}{(k_8 + k_9)k_{16}k_{15}I_{\text{PBA}}\tau(^5\text{D})\text{Tb(III)}\tau_{\text{PBA}}\text{T}\tau_{\text{PBA}}\text{S}} + \frac{1}{(k_8 + k_9)k_{16}k_{15}I_{\text{PBA}}(^5\text{D})\text{Tb(III)}_{\text{PBA}}\text{T}_{\text{PBA}}\text{S}[(^7\text{F})\text{Tb(III)}]} \quad (19)$$

where $\tau(^5\text{D})\text{Tb(III)}$, $\tau_{\text{PBA}}\text{T}$, and $\tau_{\text{PBA}}\text{S}$ are luminescence lifetime of terbium chloride, phosphorescence lifetime of PBA, and fluorescence lifetime of PBA, respectively, and are defined as $\tau(^5\text{D})\text{Tb(III)} = 1/(k_{16} + k_{17})$, $\tau_{\text{PBA}}\text{T} = 1/(k_{10} + k_{11})$, and $\tau_{\text{PBA}}\text{S} = 1/(k_7 + k_8 + k_9)$. A plot of the left-hand side of eq 19 against the reciprocal concentration of terbium chloride should result in a straight line. The ratio of the intercept to the slope of this line, $k_{15}\tau_{\text{PBA}}\text{T}$, is referred to as the triplet sensitization constant, $K_S T$.[57] Since this ratio is independent of the numerical values assigned to the luminescence, we have arbitrarily chosen a value of 1 for the luminescence intensity due to the lowest concentration of terbium chloride (5.0×10^{-4} M) and have expressed luminescences at other terbium chloride concentrations relative to this value. These relative luminescence intensities, RI values, were plotted linearly according to eq 19 (right-hand side of Figure 5), and gave 308 M^{-1} for the PBA triplet sensitization constant. The rate constant for energy transfer between PBA triplet and terbium chloride, k_{15}, was estimated from the Stokes-Einstein relationship

$$k_{15} = 8RT/3000\eta \quad (20)$$

to be 5.8×10^7 M^{-1} s^{-1} at $T = 298$ K using $\eta = 110.4$ cP for the microscopic viscosity of the 0.08 M DAP micelle in the presence of PBA and $TbCl_3$. Substituting this value for k_{15} resulted in a lifetime of micelle solubilized PBA triplet of 5.3×10^{-6} s. This value is in an excellent agreement with that determined for the lifetime pyrene triplet in aqueous micelles (5×10^{-6} s) by pulse radiolysis.[58]

In addition to appropriate spectral overlap[47] the requirement for energy transfer is that the DAP solubilized PBA triplet can diffuse to the terbium chloride, localized at the reversed micellar interior, within its lifetime. The time neded, t, for a PBA molecule to diffuse from its location to the polar interior may be estimated by the use of Fick's diffusion theory:

$$t = \frac{\bar{x}^2 3\pi\eta}{KT} \tag{21}$$

where $\bar{x}$ is the mean path length, taken as 20 Å as the PBA-$TbCl_3$ distance, η is the microscopic viscosity (110.4 cP), K is the Boltzmann constant, and T is the absolute temperature. Substituting these values into eq 21 leads to 315 ns as the time required for a PBA molecule to diffuse across the DAP headgroups to the site of $TbCl_3$. This is considerably shorter than the lifetime of the PBA triplet. The role of DAP aggregates is entirely analogous to that found for aqueous micellar SDS.[32] Both aqueous and reversed micelles compartmentalize no more than one donor molecule per aggregate and thereby obviate triplet-triplet annihilation (reaction 12). It appears that both types of micelles are effective media for increasing the efficiency of energy transfer processes.

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