The Fluorescence Response of a Structurally Modified 4-Aminophthalimide Derivative Covalently Attached to a Fatty Acid in Homogeneous and Micellar Environments

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The photophysical properties of 11-(4-*N*,*N*-dimethylaminophthalimido)undecanoic acid (DAPL), a surfactant covalently labeled with a fluorophore, in homogeneous and micellar media are reported. The remarkable sensitivity of the fluorescence properties of DAPL to the polarity of the media is attributed to the existence of a low-lying nonfluorescent twisted intramolecular charge transfer (TICT) state. DAPL is found to be an excellent fluorescence sensor for following the micellar aggregation process. Although DAPL shows enhanced binding with the micelles, the quenching experiments and the fluorescence spectral and intensity data clearly indicate that the fluorescing moiety does not penetrate into the nonpolar core region of the micelles even though the fluorophore is covalently attached to the nonpolar end group of the fatty acid. It is unambiguously established from the fluorescence data that both of the terminal groups of DAPL are located in the interfacial region of the micelles by folding of the long polymethylene chain.

1. Introduction

Fluorescent electron donor−acceptor (EDA) molecules play an important role as reporter molecules in probing the microheterogeneous environments of complex biological systems or simpler model systems such as micelles and cyclodextrins.[1−5] Design and development of new probes of this class constitutes one of the areas that continues to attract a great deal of attention from researchers because of the potential of these systems in chemical and biological applications. The preference of the EDA systems as fluorescence probes over several other classes of systems can be ascribed to exceptional sensitivity of the intramolecular charge transfer (ICT) emission properties on the polarity of the medium.[1−5] During the course of our investigations on fluorescent EDA systems,[6−13] we observed that the fluorescence properties of 4-aminophthalimide (AP) are remarkably sensitive to the polarity of the media because of the ICT nature of the emitting state.[13] Stabilization of the ICT state in polar environment results in Stokes shift of the fluorescence maximum.

The solvatochromic fluorescence response of AP is greatly enhanced in protic solvents because of the hydrogen bonding interaction of the excited state of the molecule with the solvent molecules.[13] The two features, solvatochromism and hydrogen bonding interaction, in addition to fairly high fluorescence quantum yield and lifetime, make AP an ideal fluorescence sensor for the micropolarity of an organized medium. That the fluorescence properties of AP are exceptionally sensitive to the environment is evident from the fact that AP exhibits a fluorescence spectral shift as large as 100 nm, a change in the fluorescence yield by a factor of ∼70, and a variation of the fluorescence lifetime by a factor of ∼15 on changing the solvent from 1,4-dioxane ($\epsilon = 2.21$) to water ($\epsilon = 78.3$).[13] AP has been a commonly used probe molecule for the study of solvation.[14−21] The analytical utility of *N*-methylAP in determining the water content of a medium was explored by Langhals.[22] We previously studied the microheterogeneous environments of cyclodextrins[6,7] and micellar solutions[23] by taking advantage of highly sensitive fluorescence properties of AP. The observation that AP preferentially localizes itself at the micelle−water interface allows one to measure quantitatively the polarity of the interfacial region of the micelles.[23]

A recent study of the photophysical behavior of 11-(4-aminophthalimido)undecanoic acid (APL) in micellar environment indicated that the location of the fluorescing moiety of APL in the micellar environment is very similar to that of the system without the fatty acid.[24] It was recently shown by us that when the amino hydrogens of AP are replaced by two methyl groups, the fluorescence sensitivity of the resulting system, 4-*N*,*N*-dimethylaminophthalimide (DAP), is greatly enhanced primarily for two reasons. First, in polar media, the fluorescent ICT state of DAP becomes coupled to a low-lying nonfluorescent twisted intramolecular charge transfer (TICT) state that acts as a nonradiative decay funnel. Second, the ICT state of DAP is more polar than that of AP.[13] Thus, the fluorescence probes based on the DAP fluorophore are expected to be superior to those based on AP. Moreover, dimethyl substitution of the amino hydrogens is likely to enhance the hydrophobicity of the fluorescence moiety which might encourage stronger binding of the fluorophore with the micelle, leading to deeper penetration into the core region. Because probes covalently bound to different locations of the detergents or lipids are widely employed to probe different depths of micelles and biological membranes,[1,2,25−31] it was thought that covalent attachment of the DAP moiety with the nonpolar terminal group of the fatty acid might help extract information from the core region of the micelle. With this view in mind, 11-(4-*N*,*N*-dimethylaminophthalimido) undecanoic acid (DAPL, Chart 1) was synthesized and its fluorescence response was investigated in homogeneous and micellar environments. The results show that, contrary to general expectation, the fluorophore resides in the micelle−water interfacial region.

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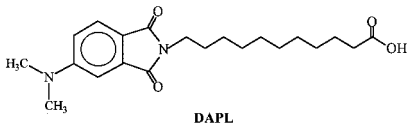
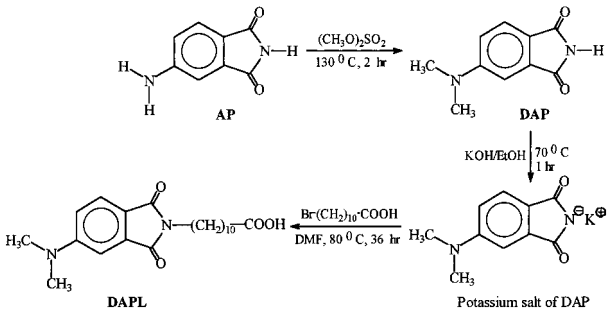
CHART 1



SCHEME 1



2. Experimental

2.1. Materials. AP (Eastman Kodak) was recrystallized from ethanol−water mixture before use. Sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB) and Triton X-100 were received from Aldrich and were purified thoroughly before use as follows. SDS and CTAB were recrystallized from ethanol−water and acetone−water mixtures, respectively. Triton X-100 was purified by column chromatography using silica gel column and acetone as eluent. Quinine sulfate monohydrate (Aldrich), used for fluorescence quantum yield measurements, was recrystallized several times from the water−ethanol mixture before use. KI and $CuSO_4 \cdot 5H_2O$, used for quenching studies, were locally procured chemicals of analytical grade. The solvents used for the measurements were rigorously purified following standard procedures.[32] Because even a trace of moisture in the solvent can affect the fluorescence properties of these EDA systems, the extent of dryness of the solvents was estimated by measuring their $E_T(30)$ values using betaine dye and comparing the measured value with the literature value.[33] The concentration of DAPL employed for the absorption and fluorescence measurements was $\sim 2 \times 10^{-6}$ M and the pH of the aqueous solution was 7 (±0.1). 11-Bromoundecanoic acid (Aldrich) was used as received for synthesis. DAPL was prepared from AP using a three-step reaction scheme. The first step involved methylation of the amino protons to obtain DAP, the second step consisted of preparation of the potassium salt of DAP, and the final step involved the attachment of the fatty acid chain. The details of the reaction conditions and the reagents are outlined in Scheme 1. The final product was purified by column chromatography (silica gel column with 30% ethyl acetate in hexane as eluent) followed by recrystallization from ethyl acetate. The compound was characterized by ^{1}H NMR and IR spectroscopy. The analytical data for the final product are as follows: IR (KBr, cm^{-1}): 3500, 2926, 2854, 1745, 1703, 1618, 1520, 1446. ^{1}H NMR ($CDCl_3$): δ 1.2−2.0 (m, 16H); 2.2 (t, 2H); 3.5 (t, 2H); 6.8 (dd, 1H); 7.1 (d, 1H); 7.6 (d, 1H).

2.2. Instrumentation. The IR and ^{1}H NMR spectra were recorded on JASCO FT-IR/5300 and Bruker ACF-200 (200 MHz) spectrometers, respectively. The absorption and fluorescence spectra were recorded using JASCO model 7800 spectrophotometer and JASCO FP-777 spectrofluorimeter, respectively. The fluorescence decay curves were measured using IBH single-photon counting spectrofluorimeter (model 5000U). The instrument was operated with a thyratron-gated flash lamp filled with hydrogen at a pressure of 0.5 atm. The lamp was operated at a frequency of 40 kHz and the pulse-width of the lamp under the operating condition was ~1.2 ns. The lifetimes were estimated from the measured fluorescence decay curves and the lamp profile using a nonlinear least-squares iterative fitting procedure. The goodness of the fit was evaluated by the χ^2 values and the plot of the residuals.

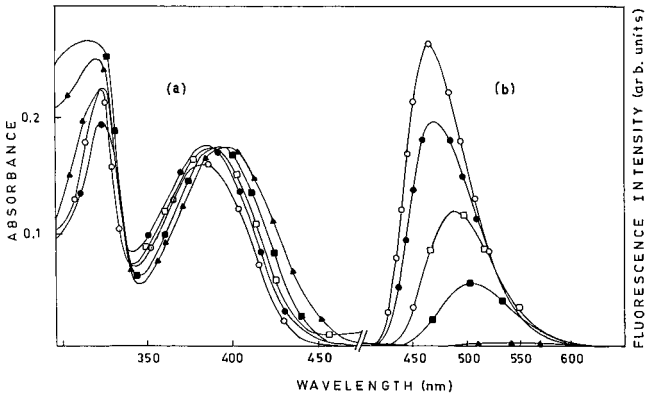


Figure 1. Absorption (a) and fluorescence (b) spectra of DAPL in various solvents: (−○−) 1,4-dioxane; (−●−) tetrahydrofuran; (−□−) acetone; (−■−) acetonitrile; (−▲−) methanol. λ_{exc} = 410 nm.

TABLE 1: Absorption and Fluorescence Spectral Properties of DAPL and APL in Solvents of Varying Polarity

		DAPL		APL[c]	
solvent	$E_T(30)$[a]	λ_{abs}^{max} (nm)	λ_{flu}^{max} [b] (nm)	λ_{abs}^{max} (nm)	λ_{flu}^{max} [d] (nm)
1,4-dioxane	35.9	384	465	355	438
tetrahydrofuran	37.2	383	469	357	442
acetone	42.5	386	488	359	459
acetonitrile	46.5	392	504	358	466
n-butanol	49.9	395	527	–	–
n-propanol	50.6	396	530	–	–
ethanol	51.9	393	532	–	–
methanol	55.1	395	535	369	527
water	63.1	417	575	369	554

[a] Measured using betaine dye. [b] Excited at 410 nm. [c] From ref 24. [d] Excited at 370 nm.

3. Results and Discussion

3.1. Photophysical Behavior in Homogeneous Media. *3.1.1. Spectral Characteristics.* DAPL displays broad absorption and fluorescence spectra typical of an ICT transition. A few representative spectra of DAPL are shown in Figure 1 and the absorption and fluorescence spectral data of DAPL in homogeneous media are collected in Table 1. To enable a comparison, the spectral data of APL are also shown in the same table. With an increase in the polarity of the medium, both the absorption and the fluorescence maxima of DAPL display a gradual red shift. However, the solvatochromic shifts of the fluorescence maxima are more pronounced than those for the absorption maxima. This behavior is indicative of an emitting state that is more polar than the ground state. This conclusion is in agreement with the fact that on electronic excitation, the dipole moment of the DAP chromophore increases by nearly 4 D.[13]

In hydroxylated solvents such as methanol and water, the Stokes shifts of the fluorescence maxima are considerably larger than those expected on the basis of the solvent polarity alone. Although this unusually large Stokes shift of the fluorescence maximum of AP in protic media has been interpreted by us[13] and others[14,15] to be due to its hydrogen bonding interaction with the solvents, a different mechanism involving solvent-mediated transfer of the imino proton of AP to the adjacent

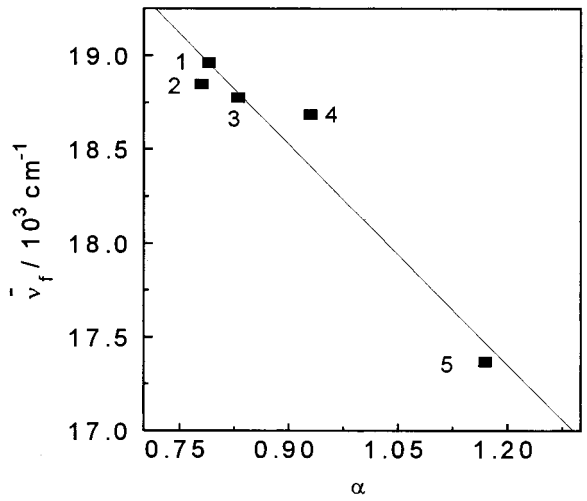


Figure 2. Plot of $\bar{\nu}_f$ (cm^{-1}) of DAPL versus α (hydrogen bonding donating parameter) (1) *n*-Butanol (0.79); (2) *n*-propanol (0.78); (3) ethanol (0.83); (4) methanol (0.93); (5) water (1.17).

carbonyl group was recently proposed.[19−21] However, this mechanism fails to account for the fact that 4-amino-*N*-methylphthalimide, a system that does not contain the imino hydrogen necessary for this solvent-mediated proton transfer, displays fluorescence properties remarkably similar to those of AP. Therefore, the hydrogen bonding interaction of the carbonyl groups of the fluorophore (hydrogen bond acceptor) and the hydroxylated solvents (hydrogen bond donor) must be responsible for the unusually high Stokes-shifted fluorescence of the AP derivatives and no proton transfer is involved in the excited state. In a recent paper, in which Pryor et al.[34] studied jet−cooled water complexes of AP and its derivatives, no proton transfer could be observed.

Note that the fluorescence peak position of DAPL bears an excellent correlation with the solvent polarity parameter, E_T-(30) in aprotic media. In protic solvents, a correlation can be observed between the wavenumbers of the fluorescence maxima and the hydrogen bond donating parameter, α,[35] of the solvents (Figure 2). In any given solvent, both the absorption and fluorescence maxima of DAPL are Stokes-shifted compared to those of APL. This is most likely due to higher ground and excited state dipole moments of the DAP moiety compared to AP. That the fluorescence peak position (one of the parameters that determines the efficiency of a polarity probe) of DAPL is more sensitive to the solvent polarity compared to APL is evident from the spectral data of the two compounds. Although DAPL exhibits a shift of the fluorescence maximum by 39 nm when the solvent is changed from dioxane ($\epsilon = 2.21$) to acetonitrile ($\epsilon = 35.94$), APL shows significantly smaller shift (27 nm) for identical change of the solvent.

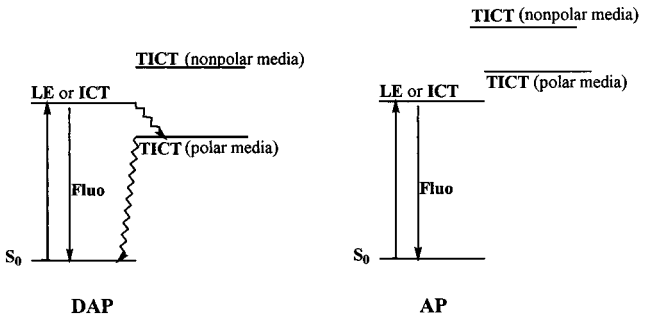
3.1.2. Fluorescence Yield and Lifetime as a Function of the Solvent Polarity. The variation of the fluorescence quantum yield (ϕ_f) and lifetime (τ_f) of DAPL with the polarity of the medium is shown in Table 2. The nonradiative rate constant [k_{nr}, calculated using $k_{nr} = (1 - \phi_f)/\tau_f$] values are also collected in Table 2. Note that while the ϕ_f, τ_f, and k_{nr} values of APL remain more or less constant in aprotic media, for DAPL, there is clearly a gradual reduction of ϕ_f and τ_f and an enhancement of k_{nr} with increase in the polarity of the media. This behavior is rationalized in Scheme 2. As the polarity of the medium is increased, the emitting state of the dimethyl-substituted chromophore gets coupled to a low-lying nonfluorescent TICT state.[36,37] In other words, the excited DAP molecules are funneled through this nonradiative channel in a polar environment. For AP derivatives, the barrier to the ICT → TICT process is large enough not to allow the molecules to follow this pathway.[13] Note that incorporation of this extra decay channel into the fluorophore through derivatization makes a significant difference in the fluorescence response of APL and DAPL. Of the three polarity indicators (the fluorescence peak position, intensity, and lifetime), the first one is controlled, as stated earlier, by the dipole moment of the emitting state and the strength of the hydrogen bonding interaction. The sensitivity of the second and the third parameters of DAPL arises largely because of the ICT → TICT decay pathway.

TABLE 2: Fluorescence Quantum Yield (ϕ_f), Lifetime (τ_f), and Nonradiative Rate Constant (k_{nr}) of DAPL in Various Solvents

solvent	ϕ_f	τ_f (ns)	k_{nr} (10^7 s^{-1})
1,4-dioxane	0.660	18.30	0.79
tetrahydrofuran	0.590	15.80	2.58
acetone	0.340	11.70	5.62
acetonitrile	0.213	7.40	10.60
n-butanol	0.037	2.50	38.90
n-propanol	0.025	2.10	47.10
ethanol	0.013	1.12	88.20
methanol	0.006	0.89	111.00
water	0.001	0.16 (73.6%)[a] 7.2 (26.4%)	640.00

[a] The relative amplitudes (R_i) were calculated using $R_i = 100B_i\tau_i/\sum_{k=1}^{2}(B_k\tau_k)$.

SCHEME 2



The data presented in Table 2 clearly suggest that DAPL performs a better role as a polarity sensor of the microenvironments than does APL. In hydrogen bond donating solvents, a drastic reduction in the fluorescence yield and lifetime is observed for both compounds. The fluorescence decay of DAPL is single exponential in all solvents except in water. A typical decay curve is shown in Figure 3. In water, we could observe a long-lived component in small percentage along with the expected short-lived major component. Because the fluorescence decay of both AP and DAP in water is single exponential, the biexponential nature of the fluorescence of APL and DAPL must be attibuted to the attached fatty acid chain. The long-lived species could arise from aggregation of DAPL. The other possibility is that an intramolecular foldback of the long polymethylene chain onto the chromophore (driven by hydrophobic forces) exists such that the carbonyl groups of the chromophore, which are usually hydrogen bonded to the water molecules, are partially shielded. Note that in the event of this foldback, the microscopic polarity around the fluorophore will be lowered and hence one can expect a long-lived emitting species (see Table 2 for trend) representing the partially shielded chromophores. Folding back of the polymethylene chain onto the fluorophore leading to intramolecular shielding of the charge transfer excited state is perhaps most clearly documented for surfactant-active rhenium(I) complexes by Reitz et al.[38,39] A

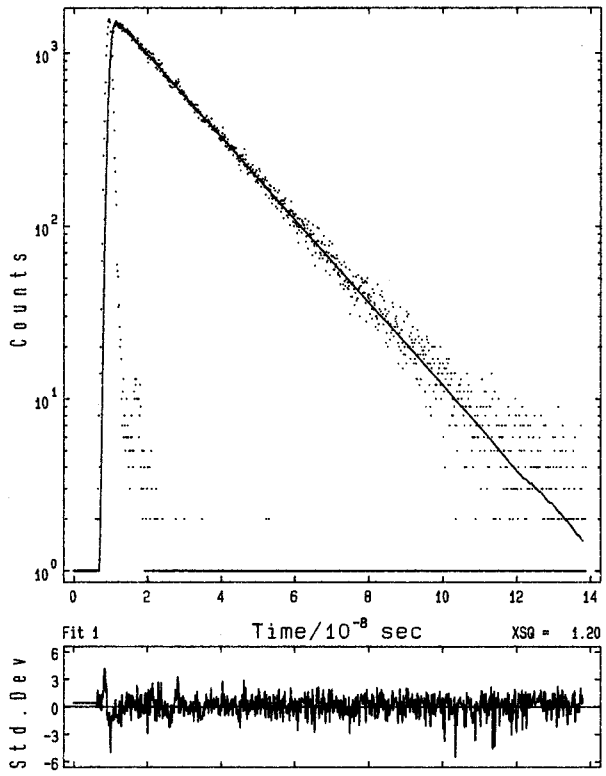


Figure 3. The exciting lamp profile, fluorescence decay curve along with the best fit to the decay curve of DAPL in dioxane. $\lambda_{exc} = 380$ nm, $\lambda_{em} = 480$ nm. The fitting parameters obtained were as follows: $\tau = 18$ ns, $\chi^2 = 1.2$.

detailed study was recently undertaken by us on a series of 1-*N*-alkylated (of different chain length) derivatives of AP specifically to determine whether self-coiling or aggregation gives rise to the second component.[40] The results indicated that the aggregates of these molecules form at very low concentration (10^{-7} M or higher) which give rise to the long-lived component in aqueous solution.

3.2. Micellar Environment. *3.2.1. Photophysical Behavior.* The polarity sensing ability of DAPL was studied using the three most commonly used micellar systems; anionic SDS, cationic CTAB, and neutral Triton X-100. When the surfactant concentration is low, the change in the fluorescence response (both spectrum and intensity) is very small. However, the fluorescence response of the system changes drastically when the surfactant concentration reaches a particular value. Obviously, this concentration represents the onset of micellar aggregation. The surfactant-induced changes in the spectral profile and fluorescence intensity are illustrated in Figure 4. Addition of surfactants leads to a blue shift of the spectrum along with an enhancement of the fluorescence intensity. On the basis of the data presented in Tables 1 and 2, these changes are to be attributed to the passage of the DAPL molecules from a highly polar aqueous to a relatively nonpolar micellar environment. A typical variation of the fluorescence intensity of the system with surfactant concentration, from which the critical micelle concentration (cmc) values are evaluated, is shown in Figure 5. The measured cmc values are collected in Table 3 along with the literature values. As can be seen, the measured cmc values are in good ageement with the literature values.

At higher surfactant concentration, when a majority of the DAPL molecules are micellized, the fluorescence intensity reaches its limiting value. Table 3 summarizes some of the fluorescence parameters corresponding to the "fully micellized" condition. The data presented in the table clearly reveal that

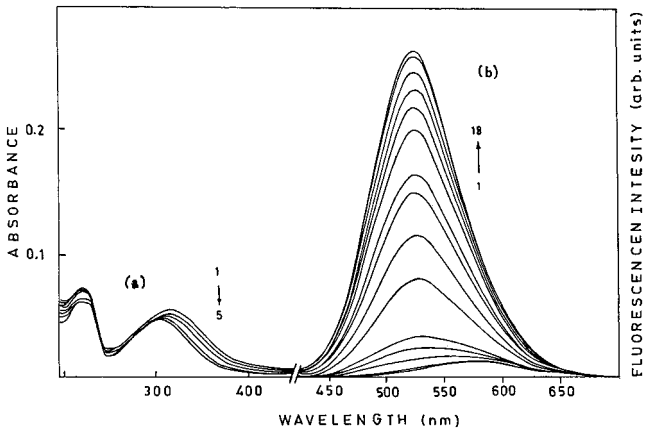


Figure 4. Absorption (a) and fluorescence (b) spectra of DAPL in aqueous solution with different amounts of Triton X-100. The concentrations of Triton X-100 (mM) (a) for the spectra labeled 1−5 are 0, 0.2, 12, 45, and 128, respectively; (b) in increasing order of intensity, 0, 0.06, 0.13, 0.2, 0.27, 0.4, 0.7, 0.9, 3.7, 6.5, 9.2, 12, 23, 34, 45, 62, 111, 128, respectively. $\lambda_{exc} = 410$ nm.

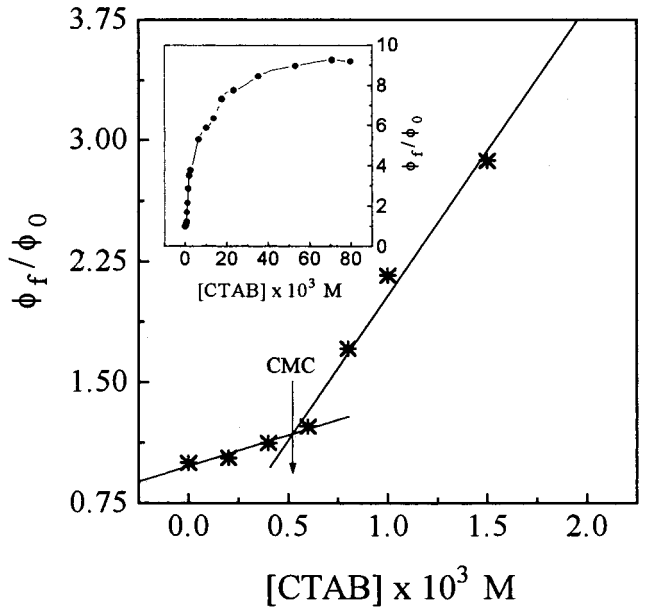


Figure 5. A plot of relative fluorescence intensity of DAPL (ϕ_f/ϕ_0) as a function of CTAB concentration in aqueous solution. The insert shows the variation of the ratio over a larger concentration range.

TABLE 3: Fluorescence Spectral Shift and Enhancement of DAPL Corresponding to the Fully Micellized Condition; the Measured cmc and Lifetime Values Are Also Shown

surfactant	concentration (mM)	maximum ϕ_f/ϕ_0	maximum shift (nm)	cmc (mM) literature[a]	cmc (mM) measured	τ_1 (ns) $(R_1)^b$
SDS	75	7.2	31.0	8.00	7.4	0.56 (97.2)
CTAB	80	9.2	44.5	0.92	0.6	0.34 (98.7)
Triton X-100	128	22.4	54.0	0.26	0.27	0.81 (96.8)

[a] From ref 1. [b] Calculated using relative amplitude, $R_i = 100B_i\tau_i/\sum_{k=1}^{2}(B_k\tau_k)$.

DAPL displays much higher fluorescence enhancement and spectral shift on micellization compared to APL.

3.2.2. The Binding Constant. A quantitative estimate of the binding of DAPL with the micelles was obtained from the fluorescence intensity data. Because the fluorescence intensity

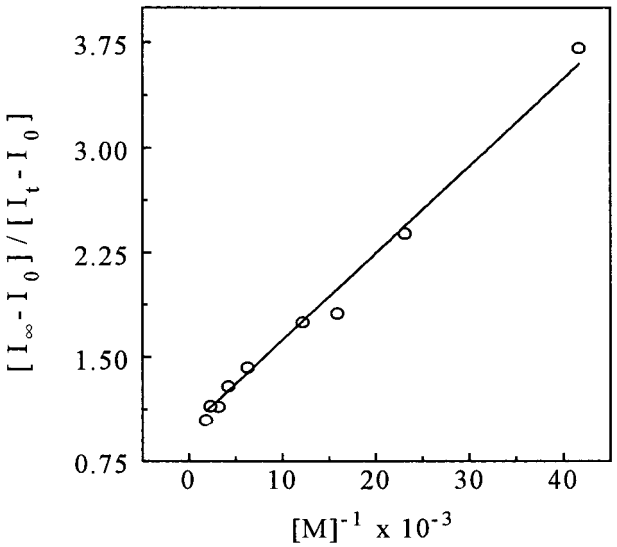


Figure 6. Plot of $(I_\infty - I_0)/(I_t - I_0)$ against $[M]^{-1}$ in Triton X-100 for DAPL.

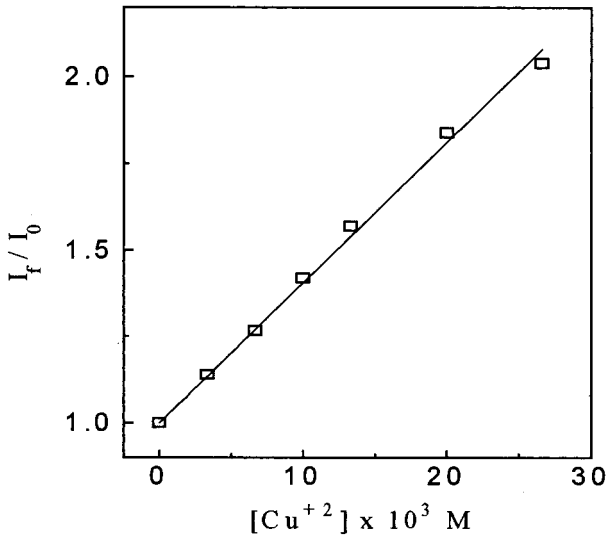


Figure 7. Plot of relative fluorescence intensity of DAPL in SDS micellar environment (75 mM) as a function of the concentration of Cu^{+2}.

of the probe molecule in aqueous and micellar environment differ significantly, we used for the estimation of the binding constant (K) the equation suggested by Almgren et al.[41] According to this,

$$\frac{I_\infty - I_0}{I_t - I_0} = 1 + (K[M])^{-1} \quad (1)$$

where I_∞, I_0, and I_t are the relative fluorescence intensities under complete micellization, in the absence of micellization, and in presence of intermediate amounts of surfactant, respectively. [M] represents the concentration of the micelle which is given by $[M] = ([sur] - cmc)/N$, and [sur] represents the surfactant concentration and N is the aggregation number of the micelle. The N values used in the calculation of [M] are 62 for SDS, 60 for CTAB, and 143 for Triton X-100. A typical plot based on the above in aqueous micelles is shown in Figure 6. The measured K values (±15%) for DAPL are 17 000, 18 000, and 24 000 M^{-1} for SDS, CTAB, and Triton X-100, respectively. These K values are four- to fivefold higher than those obtained for the bare fluorophore (AP) and two- to fourfold higher relative to APL. Therefore, covalent attachment of the fatty acid chain and dimethyl functionalization of the amino group clearly result in stronger binding of the fluorescence probe molecule with the micelle.

3.2.3. Fluorescence Quenching Studies. To probe the location of the fluorescing moiety in the micellar environment we studied the fluorescence quenching behaviour of fully micellized DAPL using ionic quenchers, I^- and Cu^{2+}. The idea behind these measurements is that because these quenchers are accessible only in the aqueous and interfacial region of the micelle, the fluorescence quenching data are expected to be useful in determining whether the fluorescing moiety is located in these regions or in the deeper nonpolar core region. The quenching measurements were also performed with the bare fluorophore, DAP in both aqueous and micellar media. The plots of the relative fluorescence intensity versus the quencher concentration were found to be linear indicating negligible static quenching over the concentration range used in the experiments. A typical quenching plot is illustrated in Figure 7 and the quenching data for DAP and DAPL are collected in Table 4.

The data presented in Table 4 illustrate that both I^- and Cu^{+2} are good quenchers of DAP and DAPL fluorescence in aqueous medium. The quenching rates of DAP and DAPL with I^- in cationic micellar environment (CTAB) and with Cu^{2+} in anionic micellar medium (SDS) are considerably higher presumably owing to high local concentration of the quencher ions near the surface because of electrostatic attraction. In neutral micellar medium (Triton X-100) where electrostatic forces are absent, the quenching rate constant is lower than that observed in aqueous medium, suggesting lesser accessibility of probe molecules toward the quenchers. The quenching experiments clearly suggest that the fluorescing moiety of DAPL is accessible to aqueous quenchers. Moreover, the similarity of the quenching data of DAPL and DAP indicates that the location of fluorescing moiety in the former system is very similar to that of the latter system in micelles.

TABLE 4: Fluorescence Quenching Data of DAP and DAPL in Aqueous and Micellar Media

		k_q[a]/10^9 M^{-1} s^{-1}			
probe	quencher	H_2O	SDS	CTAB	Triton X−100
DAP	Cu^{+2}	16.2	66	−	2.33
	I^-	11.9		118	−
DAPL	Cu^{+2}	18.3	64	−	2.62
	I^-	8.1		81.6	−

[a] The uncertainties in k_q values are fairly high because τ_0 values were low (~0.2 ns) and could not be measured accurately with the experimental setup used in this study.

3.3. The Location of the Fluorophore. That the fluorescing moiety of DAPL occupies a less polar site (compared to water) in micellar media is evident from the fluorescence properties of DAPL. However, the results of the quenching experiments suggest that the fluorophore is accessible to water. The purpose of the attachment of the fluorophore with the nonpolar terminal of the fatty acid chain was not only to enhance the binding interaction but also to ensure that the fluorophore penetrates into the deeper core region of the micelle. Using pyrene-linked amphiphiles, Zachariasse showed that as the length of the fatty acid chain increases the polarity of the binding site of the probe decreases.[27] Turro et al. showed with the use of indole-linked detergents that the fluorophore (indole moiety) resides in the interior of the host micelles in contrast to the native fluorophore.[28,29] Several *n*-(9-anthroyloxy) fatty acids were employed extensively to probe different depths of the micelle.[30,31] It was found that the fluorophores of the fatty acids reside at graded

series of positions in the micelle depending on the location where the fluorophore is connected with the fatty acid.[30] The fluorophore was found to be located 15 Å from the head group, i.e., near the center of the micelle when it is attached at 12th position of the hydrocarbon chain of the fatty acid. Recently, this probe was used to monitor the water content inside micelles.[31] Although, as expected, the binding interaction increases significantly, the fluorophore resides more or less in the vicinity of interfacial region of the micelle. Apart from the quenching data, this is also evident from the fluorescence intensity and spectral shift parameters. Penetration into the core region of the micelle would have led to a spectral shift of nearly 100 nm (see Table 1, assuming the core polarity to be similar to that of 1,4-dioxane) and intensity enhancement of ~600-fold. The maximum spectral shift and enhancement observed in micellar media, which lie between 31 and 54 nm and 7 and 22, respectively, are far less than the expected values for a 1,4-dioxane-like polar core region. We are thus led to believe that covalent attachment of the fluorophore at the terminal hydrocarbon chain of the fatty acid does not lead to incorporation of the fluorescing moiety into the core region of the micelle. Strong hydrogen bonding tendency of the carbonyl groups of the fluorophore is perhaps responsible for the fluorophore's location at the interface. A situation where both the terminal groups of DAPL are located at the interface can only be achieved by folding of the long hydrocarbon chain of the molecule.

4. Conclusion

Dimethyl functionalization of AP that opens up an additional decay channel for the emitting state of the molecule enhances the sensitivity of the fluorescence parameters remarkably. DAPL is proved to be a potential indicator to follow the micellar aggregation process irrespective of the charge of the micelle. Although DAPL binds more strongly with the micelles, presumably because of enhanced hydrophobicity of the fluorophore, the location of the fluorophore as determined from the fluorescence data is not very different from that observed with bare AP or DAP. The folding of the polymethylene chain in micellar media seems to be a common behavior exhibited by aminophthalimide-labeled derivatives. Because the hydrogen bonding interaction of the fluorescing moiety with water molecules is responsible for this particular arrangement of the fluorophore in micellar environment, it is evident that unless this interaction is somehow blocked it is not possible to incorporate the fluorophore into the core region of the micelle.

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