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Phase-Transfer Catalyst-Induced Changes in the Absorption and Fluorescence Behavior of Some Electron Donor−Acceptor Molecules

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Abstract: The quaternary ammonium salts find extensive use in a variety of chemical applications as surfactants and phase-transfer catalysts. Even though the interaction of the surfactants with various systems has been studied rather extensively, very little information is available on how the phase-transfer catalysts (PTC) interact with the dipolar systems in nonpolar media and how/whether these solubilizing agents affect the properties of the dissolved molecules. In this paper, the interaction of several tetraalkylammonium salts, commonly used as PTC, with a number of electron donor−acceptor (EDA) systems has been studied by absorption and fluorescence spectroscopy. The phase-transfer catalysts have been found to affect both the absorption and fluorescence properties of the EDA systems. The spectral changes of the EDA molecules induced by the tetraalkylammonium salts suggest the formation of an 1:1 complex between the two in nonpolar media. An electrostatic interaction between the phase-transfer catalysts (which exist as ion pairs in nonpolar media) and the dipolar molecules is shown to be the driving force for the formation of the complex. The dependence of the formation constant of the complex on the polarity of the media suggests a charge-transfer nature of the complex. It is shown that the anionic component of the salts serves as a source of electron to the positive end of the dipolar molecule, while the tetraalkylammonium cation, besides helping solubilization of its anionic counterpart in the nonpolar media, serves neutralizing the negative charge at the acceptor end of the EDA molecule. In effect, a cooperative influence of the cationic and anionic components of the PTC enhances the charge separation within the dipolar fluorophores. On the basis of the PTC-induced changes in the photophysical behavior of the EDA molecules, a possible structure for the 1:1 complex has been proposed. It has been concluded that a phase-transfer catalyst should not be treated as an innocuous substance that merely helps transfer of a polar substance from a polar to a nonpolar environment. Instead, it is demonstrated that the association of a PTC with a dipolar species can significantly change various properties of the latter.

Introduction

The quaternary ammonium salts are extensively used in chemical applications as surfactants[1−9] and as well as phase-transfer catalysts.[10−21] Tetraalkylammonium halides with one or two large alkyl groups, such as cetyltrimethylammonium bromide (CTAB), are good surfactants that, when added to a two-phase aqueous−organic system, normally produce micelles in aqueous medium. On the other hand, small quaternary salts (e.g., tetrabutylammonium halides) and large ones (e.g., tetraoctylammonium halides) with all four identical alkyl chains are poor surfactants, but good phase-transfer catalysts. These salts are used to bring closer two otherwise insoluble reactants in proper concentration to get a faster reaction rate.[10,11] In a binary two-phase solution, a good phase-transfer catalyst like tetrabutylammonium bromide (TBAB) circulates between the two phases across the interface instead of staying in a single phase like micelles. These phase-transfer catalysts are generally less stable in aqueous medium. In nonpolar media, they are highly soluble and known to exist as ion pairs. Having a quaternary cation with long hydrophobic chains, a phase-transfer catalyst entails the extraction of ionic or highly polar molecules into an organic solvent or their solubilization therein. Interestingly, even though the utility of the phase-transfer catalysts in

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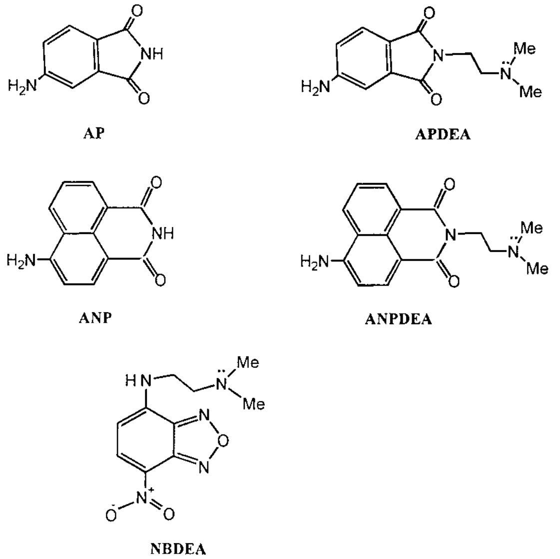
synthetic chemistry is rather well documented,[13] not much attention has been paid to understanding the exact nature of the binding of these salts with polar organic molecules in a nonpolar medium. We take note of the fact that some studies have been reported where the behavior of a phase-transfer catalyst in the bulk phase (as is the present study) has been investigated using various techniques such as UV−visible and NMR spectroscopies.[15−18,20] Recently, the interfacial behavior of a phase-transfer catalyst associated with a phenoxide ion was studied using a laser scattering method.[22] In another recent paper, Thomas and Kamat made use of a phase-transfer catalyst to prepare and study the behavior of stable gold nanoparticles in a nonpolar medium.[23] In this paper, we address ourselves to a fundamental question of finding out whether the role of the phase-transfer catalysts lies merely in helping the solubilization of a polar system in nonpolar media to facilitate its reaction with a third substance in an organic medium. Specifically, we attempt to find out the exact nature of the interaction of the phase-transfer catalysts with neutral polar organic systems and to what extent the phase-transfer catalysts change the original properties of the solubilized systems.

To achieve this objective, we have chosen some fluorescent electron donor−acceptor (EDA) systems as the probe molecules. Since the absorption and fluorescence behavior of the chosen systems is mainly controlled by a low-lying intramolecular charge-transfer (ICT) state,[24−32] whose location is extremely sensitive to the surrounding medium, it is expected that the changes in the absorption and fluorescence properties of these systems induced by the phase-transfer catalysts will provide information on how the ion pairs interact with the probe molecules. Five different EDA systems have been chosen for this purpose. Among the chosen systems (Chart 1), 4-aminophthalimide (AP) and 4-amino-1,8-naphthalimide (ANP) are highly fluorescent systems which emit from a ICT state.[24−28,30,33] The location of this state is highly dependent on the polarity of the media and on the hydrogen bond-donating ability of the solvent molecules. APDEA and ANPDEA are three-component systems comprising an AP or ANP moiety as the fluorophore, a dimethylene group as the spacer, and a dimethylamino moiety as the guest-binding site. It should be noted that APDEA and ANPDEA not only possess most of the features of the parent systems (AP and ANP) but, in addition, contain a site specifically suited for the binding of the cations.[30] NBDEA is a similar system except that it contains a dimethylaminonitrobenzoxadiazole moiety as the fluorophore. The solvent-sensitive fluorescence properties of the NBD derivatives and the ability of NBDEA in sensing various metal ions are well documented.[29,31,32] The fundamental difference in the photophysical properties of the parent systems and the multicomponent systems is that the former set of molecules is highly fluorescent (at least in the nonpolar media) while the latter is not. The low fluorescence quantum yield of the three-component systems is shown to be due to *through-space* photoinduced intramolecular electron transfer (PIET) between the two terminal moieties of the molecules.[30−32,34] We have also examined the effect of the tetraalkylammonium salts on a few other systems (NP and MNP) that do not possess the strong electron-donating amino group at the 4-position and NPDEA, which comprises NP as the fluorophore but contains the additional site for the cation binding. These structures have been shown in Chart 2. We thought that a study of the effect of the phase-transfer catalysts on these systems and a comparison of the behavior of these systems with those shown in Chart 1 would help in understanding the exact role of the catalysts and in obtaining an answer to the question raised above.

Chart 1

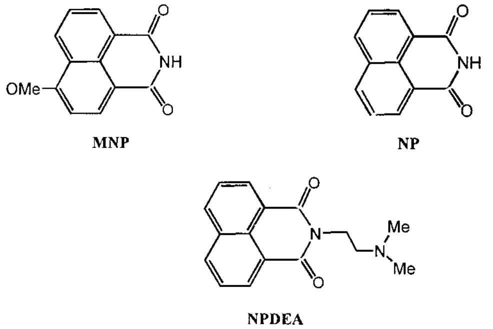


AP APDEA

ANP ANPDEA

NBDEA

Chart 2



MNP NP

NPDEA

Experimental Section

AP (Acros Organics) and ANP (Aldrich) were recrystallized twice from ethanol and used for spectroscopic measurement. APDEA, ANPDEA, and NBDEA were prepared by following the previously reported procedures.[30,32,34] The column-purified compounds were sometimes recrystallized from absolute ethanol for further purification. Various solvents used in this study (such as toluene, 1,4-dioxane, acetonitrile, cyclohexane, and ethanol) were all purified rigorously by following the standard procedures.[35] Triply distilled water was used for spectroscopic measurements in aqueous solutions. Five different

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phase-transfer catalysts have been used. Tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBAC), tetraoctylammonium bromide (TOAB), tetrabutylammonium iodide (TBAI), and tetrabutylammonium perchlorate (TBAP) were procured from Aldrich and used without any purification.

Dilute solutions of the probe molecules were used for both absorption and fluorescence measurements. The optical densities of the solutions employed for spectrophotometric and spectrofluorometric measurements were maintained between 0.1 and 0.2 at the longest wavelength absorption maximums. This corresponded to a concentration between 2 and 8 × 10^{-5} M. A measured amount of tetraalkylammonium salts was added directly to a 2.5-mL solution of the compound taken in a cuvette for studying the salt effect.

The absorption and fluorescence spectra were recorded on a Shimadzu UV−visible−NIR spectrophotometer (model UV-3101PC) and a Jasco spectrofluorometer (model FP-777), respectively. The fluorescence decay curves were recorded using an IBH single photon counting spectrofluorometer (model 5000). 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 conditions was ∼1.2 ns. The lifetimes were estimated from the measured fluorescence decay curves and the lamp profiles using a nonlinear least-squares iterative fitting procedure. The goodness of the fit was evaluated from the χ^2 values and the plot of the residuals.

The molecular structures of the fluorophores and their dipole moments were obtained through quantum chemical calculations based on semiempirical method. The AM1 (Austin model 1) method was used for this purpose in view of its superiority over other semiempirical methods.[36−38]

Results

Absorption. The effect of TOAB on the UV−visible absorption spectrum of AP is illustrated in Figure 1. With progressive addition of TOAB, the long-wavelength charge-transfer band of AP, which shows a maximum at around ∼350 nm in toluene, shifts gradually toward red with a gain in intensity in the longer wavelength region. An isosbestic point could be observed at ∼350 nm. The spectral changes clearly indicate 1:1 complexation between AP and TOAB. The spectral maximum of the first absorption band of AP on complexation with TOAB is found to be ∼20 nm red-shifted (measured in the presence of 4.4 mM TOAB) relative to its original position. A similar observation could be made in the presence of TBAB and TBAC. The spectral shifts observed in the presence of TBAB and TBAC are ∼12 and ∼30 nm, respectively, in toluene. The three-component system, APDEA, which contains AP as the fluorophore moiety with an additional cation binding site, shows a very similar behavior. The spectral data of this system in the presence and in absence of various phase-transfer catalysts are collected in Table 1. It is quite important to note in this context that in the presence of TBAI and TBAP no significant change in the absorption behavior of AP or APDEA could be observed.

The absorption behavior of ANP and ANPDEA in the presence of the TOAB (depicted in Figure 2) also indicates 1:1 complexation between these systems and TOAB. The spectral data for the two systems in the presence of other phase-transfer catalysts are indicated in Table 1. NBDEA also exhibits a Stokes shift of the absorption maximum in the presence of the tetraalkylammonium salts, and the magnitude of the shift lies between 12 and 25 nm (Table 1). In this case, even though 1:1 complexation is indicated for a lower concentration of TOAB, higher order complexes could be observed (from the loss of isosbestic point) at higher concentrations of the salt.

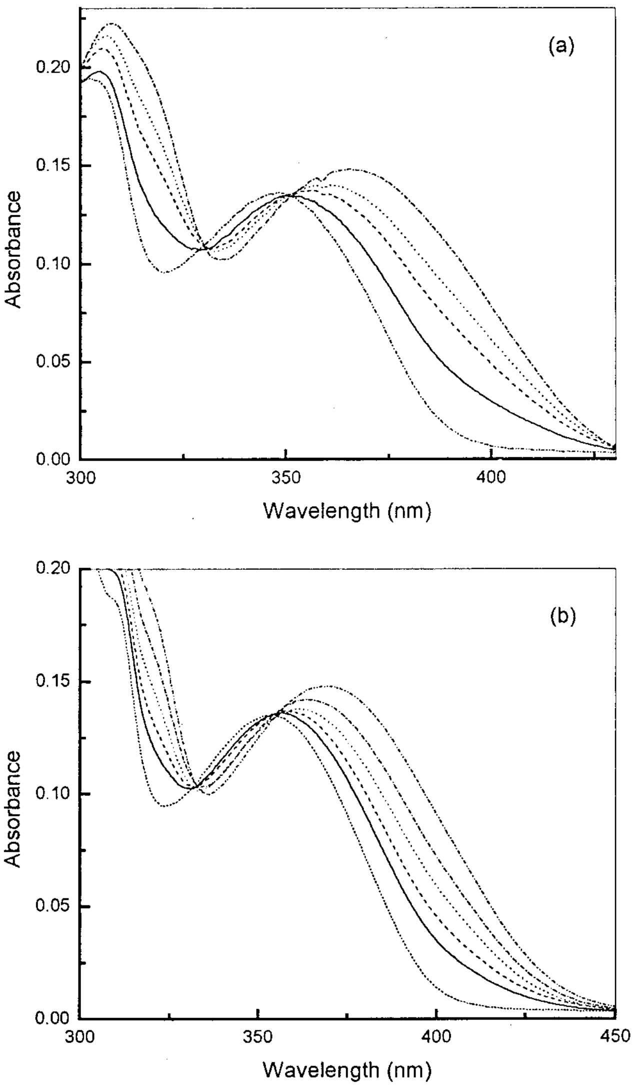

Figure 1. Effect of TOAB on the UV−visible absorption behavior of AP (a) and APDEA (b) in toluene. The concentration of TOAB (in mM) in increasing order of absorbance at the longest wavelength maximums are 0, 0.66, 1.46, 2.19, and 4.39 in (a) and 0, 0.37, 0.66, 1.39, 2.27, and 4.54 in (b).

The other observations can be summarized as follows: First, even though spectral changes similar to what have been described above could be observed for all the systems shown in Chart 1, in other nonpolar solvents such as cyclohexane, no noticeable spectral change could be observed for these systems in polar solvents such as acetonitrile, ethanol, or water. In 1,4-dioxane ($E_T(30) = 36.0$),[39] which is slightly more polar than toluene ($E_T(30) = 33.9$),[39] the complexation could be observed, though not as prominently as in the case of toluene. Moreover, in this solvent, the general trend was that the isosbestic point observed initially could not be seen for higher concentration of the salts. Second, none of the systems exhibit any significant changes in spectral behavior (even in nonpolar media) with phase-transfer catalysts such as TBAI or TBAP. Third, for systems such as NP and MNP, which do not contain the amino group at the 4-position, no spectral changes could be observed with the tetraalkylammonium salts employed in this study. Moreover, it is found that NPDEA, which contains the cation

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Table 1. Absorption and Fluorescence Spectral Maximums (in nm) Observed for Various Systems (in Toluene) in the Presence of Different Tetraalkylammonium Salts[a]

	none		TOAB		TBAB		TBAC	
system	λ_{max}(abs) (nm)	λ_{max}(flu) (nm)	λ_{max}(abs) (nm)	λ_{max}(flu) (nm)	λ_{max}(abs) (nm)	λ_{max}(flu) (nm)	λ_{max}(abs) (nm)	λ_{max}(flu) (nm)
AP	350	430	370	467	362	503	379	520
APDEA	353	430	379	502	380	504	380	515
ANP	403	469	420	520	434	522	424	533
ANPDEA	403	470	436	522	427	521	445	540
NPDEA	345, 332	370, 397	345, 332	370	345, 331	370	345, 332	370
NBDDEA	445	517	455	525	471	533	470	540

[a] A ~2 × 10^{-5} M solution of the compounds in toluene was used in room temperature; the concentrations of the phase-transfer catalysts were ~1.7 mM in the case of TBAC and 4.4 mM for the other salts; λ_{ex} = 350 nm for AP, APDEA, 305 nm for NPDEA, 380 nm for ANP and ANPDEA, and 415 nm for NBDEA.

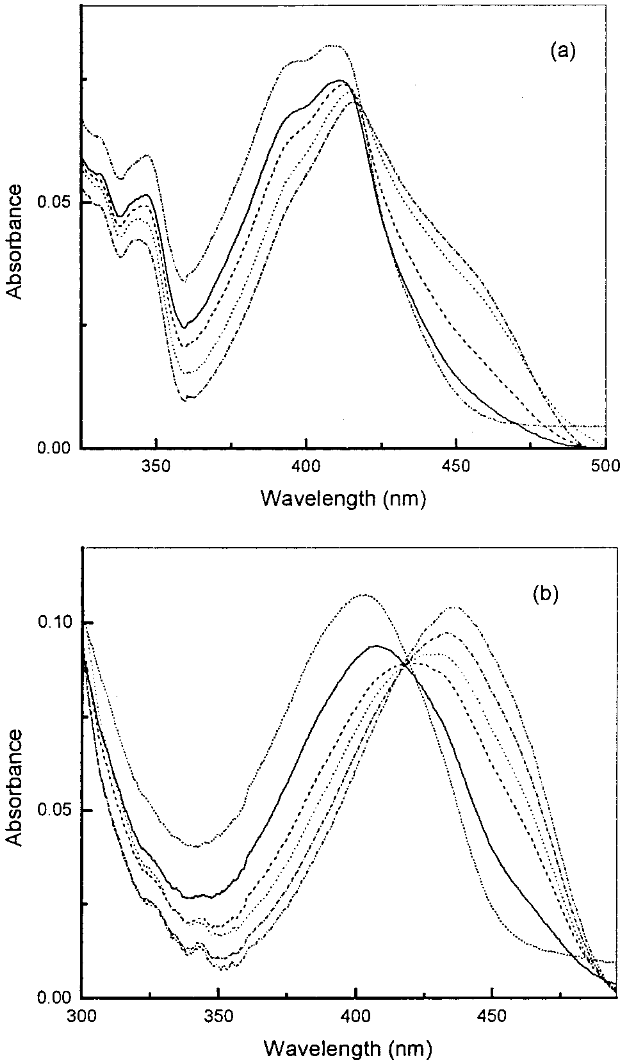

Figure 2. Effect of TOAB on the UV−visible absorption behavior of ANP (a) and ANPDEA (b) in toluene. The concentration of TOAB (in mM) in increasing order of the absorbance at the longest wavelength maximums are 0, 0.15, 0.44, 0.88, and 1.54 in (a) and 0, 0.29, 0.88, 1.09, 1.83, and 3.73 in (b).

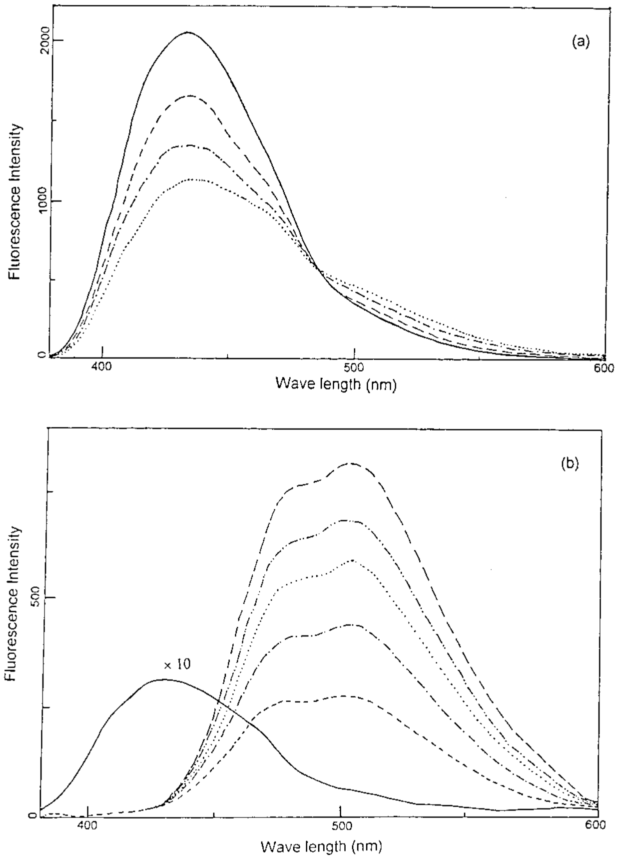

Figure 3. Effect of TOAB on the fluorescence behavior of AP (a) and APDEA (b) in toluene. TOAB concentrations (in mM) are 0 (−), 0.51 (- - -), 1.02 (- • -), and 1.46 (••••) in (a) and 0 (−), 0.66 (- - -), 1.39 (- • -), 2.27 (•••••), 3.07 (- • • -), and 4.54 (- -) in (b). AP and APDEA were excited at 335 and 345 nm, respectively.

binding site but is devoid of the amino group at the 4-position of the ring, does not exhibit any shift of its absorption maximum in the presence of the phase-transfer catalysts in nonpolar media.

Steady-State Fluorescence. Systems comprising AP, ANP, and NBD moieties are known to display fairly broad structureless intramolecular charge-transfer fluorescence extremely sensitive to the surrounding environment. Further, the sensitivity of the fluorescence properties of these systems is much more pronounced compared to their absorption properties. This is due to the fact that electronic excitation leads to an increased separation of the charge (between the amino group and the electron-withdrawing C═O or NO_2 group) in these fluorophores. In toluene, AP exhibits a strong fluorescence band with a maximum at ~427 nm. On addition of TOAB, this fluorescence gets quenched and a relatively weak new emission band appears at a longer wavelength (Figure 3). The existence of an isosbestic point confirms 1:1 complexation between the fluorescence probe molecules and the phase-transfer catalysts. The peak positions of the new emission in the presence of 1.7 mM TOAB, TBAB, and TBAC are at 475, 503, and 520 nm, respectively.

While a similar behavior is noticed in the case of ANP, the multicomponent systems (APDEA, ANPDEA, NBDEA) behave slightly differently. For the latter systems, the quenching of the

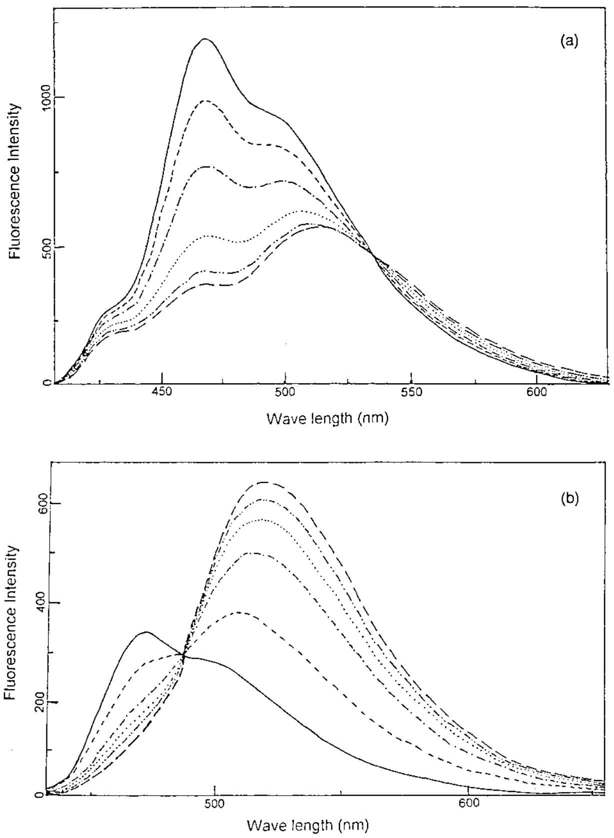

Figure 4. Effect of TOAB on the fluorescence behavior of ANP (a) and ANPDEA (b) in toluene. TOAB concentrations (in mM) are 0 (−), 0.15 (- - -), 0.44 (- • -), 0.88 (••••), 1.54 (- • • -), and 1.98 (- -) in (a) and 0 (−), 0.29 (- - -), 0.88 (- • -), 1.09 (••••), 1.46 (- • • -), and 1.83 (- -) in (b). ANP and ANPDEA were excited at 380 nm.

original fluorescence was associated with a dramatic enhancement of the fluorescence intensity of a new emission. The new fluorescence band was found to be drastically Stokes-shifted (as large as 90 nm) relative to the original fluorescence (Figure 4). The degree of enhancement of the fluorescence intensity (relative to the original fluorescence) was found to be as large as 25-fold.

The other observations that have been made are as follows: First, the changes in the fluorescence behavior of the systems as stated above could also be observed in other nonpolar solvents such as cyclohexane. In relatively more polar solvent, 1,4-dioxane, the new emission was found to be much weaker compared to that observed in toluene. However, in polar media, no noticeable changes in the fluorescence behavior could be observed in the presence of the tetraalkylammonium salts. In the case of NP, MNP, and NPDEA, no significant change in the fluorescence behavior of these systems could be observed even in a nonpolar environment. TBAI and TBAP were found to have no significant influence on the fluorescence behavior of any system shown in Charts 1 and 2 even in the nonpolar media.

Fluorescence Excitation. Fluorescence excitation spectra were recorded for all the systems monitoring the original fluorescence as well as the Stokes-shifted fluorescence band with a view to identifying the origin of the new fluorescence. The excitation maximum obtained on monitoring the longer wavelength fluorescence band is found to be distinctly Stokes-shifted relative to that obtained on monitoring the original fluorescence band. However, the excitation maximum corresponding to the longer wavelength fluorescence band resembles very closely the absorption peak of the system in the presence of the tetraalkylammonium salts. This suggests that the new emission originates from the ground-state complex formed between the salts and the probe molecules. A typical fluorescence excitation spectrum is shown in Figure 5.

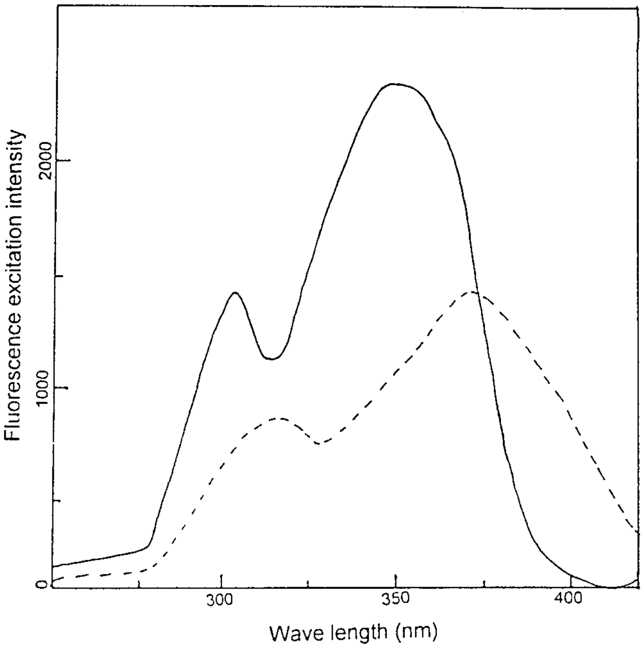

Figure 5. Effect of TOAB on the fluorescence excitation spectrum of AP in toluene. TOAB concentrations are 0 (−) and 4.39 $\times 10^{-3}$ M (- - -). The monitoring wavelength was 430 and 467 nm, respectively.

Fluorescence Decay Behavior. The fluorescence decay behavior of the systems has also been investigated with a view to obtaining further details on the nature of the interaction between the phase-transfer catalysts and the fluorescent systems. The fluorescence decay behavior has been studied both in the absence and the presence of the salts. In the latter case, the decay curves have been measured by monitoring the original fluorescence as well as the new fluorescence band. The decay parameters obtained for various systems in toluene and 1,4-dioxane are collected in Table 2. Some representative decay profiles depicting the influence of a phase-transfer catalyst along with the best fit to the decay are shown in Figure 6. The main features of the decay behavior can be summarized as follows:

AP possesses a fairly long fluorescence lifetime (τ) in aprotic media.[25] As can be seen from Table 2, the major component has a lifetime between 13 and 17 ns in toluene and 1,4-dioxane. In the presence of TOAB (4.4 mM), the τ values are reduced marginally to 11−12 ns. A similar behavior could be observed in the case of ANP, whose lifetimes (8.8 and 11.1 ns in toluene and 1,4-dioxane, respectively) are lowered to 8.3 and 9.0 ns.

In contrast to AP, the major component of the decay in the case of the three-component system, APDEA is a very short-lived species.[30] This is due to the PIET quenching of the fluorescence. On addition of TOAB, an increase in the τ values of the short-lived component could be observed. Since, in the case of ANPDEA, PIET is not very significant,[30] the major component has a comparatively longer lifetime and the influence of TOAB on this value is rather small. In the case of NBDEA, the influence of TOAB on the τ values of the major component of the decay is not very significant.

Discussion

Phase-Transfer Catalysis. A PTC reaction is essentially a two-phase reaction between salts usually in aqueous form and

Table 2. Fluorescence Decay Parameters[a] for the Systems Studied in the Absence and in the Presence of TOAB (∼4 mM) in Toluene and 1,4-Dioxane

substance	solvent	lifetimes[b] (ns) without TOAB	lifetimes[b] (ns) with TOAB at short λ.[c]	at long λ[c]
AP	toluene	3.9 (0.03)	2.7 (0.06)	3.2 (0.03)
		13.4 (0.08)	11.2 (0.06)	12.2 (0.09)
	1,4-dioxane	16.9 (0.07)	1.5 (0.03)	13.5 (0.08)
			12.2 (0.07)	
APDEA	toluene	0.1 (5.75)	0.5 (0.35)	2.9 (0.07)
		13.3 (0.01)	9.4 (0.02)	12.8 (0.05)
	1,4-dioxane	0.2 (1.84)	0.7 (0.22)	2.7 (0.08)
		17.5 (0.004)	12.0 (0.04)	13.1 (0.04)
ANP	toluene	1.6 (0.06)	1.9 (0.13)	8.5 (0.11)
		8.8 (0.08)	8.3 (0.03)	
	1,4-dioxane	11.1 (0.11)	9.0 (0.11)	9.9 (0.11)
ANPDEA	toluene	2.1 (0.17)	1.9 (0.17)	1.9 (0.07)
			4.4 (0.01)	8.1 (0.06)
	1,4-dioxane	3.3 (0.12)	2.3 (0.09)	3.1 (0.06)
		5.3 (0.03)	7.1 (0.05)	8.6 (0.08)
NBDEA	toluene	0.3 (0.91)	0.3 (0.79)	0.3 (0.61)
		6.4 (0.01)	6.7 (0.01)	7.1 (0.01)
	1,4-dioxane	0.2 (1.56)	0.6 (0.36)	1.2 (0.19)
		10.2 (0.03)	5.3 (0.01)	14.7 (0.02)

[a] Decay curves were fitted to a single-exponential/biexponential function, depending on the quality of the plot of the residuals and the χ^2 values. [b] ±10% for values higher than 1 ns and 15−20% for values lower than 1 ns; the quantities shown within parentheses are the preexponential factors. [c] The short wavelength corresponds to 400, 450, and 495 nm for AP, ANP, and NBD derivatives; the long wavelength corresponds to 480, 540, and 555 nm, respectively.

substrates in organic solvents in the presence of a phase-transfer catalyst. A simple PTC reaction, halide displacement reaction, for example, can be best represented by

$$\mathrm{RX_{org}} + \mathrm{Y_{aq}}^- \xrightarrow{\mathrm{PTC}} \mathrm{RY_{org}} + \mathrm{X_{aq}}^-$$

This reaction actually consists of two steps; an extraction step

$$[\mathrm{Q^+X^-}]_{\mathrm{org}} + \mathrm{Y_{aq}}^- \Leftrightarrow [\mathrm{Q^+Y^-}]_{\mathrm{org}} + \mathrm{X_{aq}}^-$$

and the chemical reaction step

$$[\mathrm{Q^+Y^-}]_{\mathrm{org}} + \mathrm{RX_{org}} \rightarrow [\mathrm{Q^+X^-}]_{\mathrm{org}} + \mathrm{RY_{org}}$$

where Q^+ stands for the quaternary ammonium cation.

Clearly, the role of the phase-transfer catalyst (Q^+) is simply to assist the transfer of the anion, Y^-, from the aqueous phase to the organic phase to enhance the reaction rate in the latter phase.

Formation Constant (*K*) of the Complexes. The phase-transfer catalyst-induced changes in the absorption behavior of the systems depicted in Chart 1 indicate the formation of an 1:1 complex in the ground state in nonpolar media. The formation constants of the complexes have been evaluated from both the absorption and fluorescence data using the following procedures:

The 1:1 complexation of two species (A stands for the probe, and B stands for the phase-transfer catalyst) can be indicated as

$$\mathrm{A} + \mathrm{B} \Leftrightarrow \mathrm{C} \tag{1}$$

where C stands for the complex.

The equilibrium concentration of the species (indicated by the subscript, e) and their total concentration (indicated by the subscript, t) are related as

$$[\mathrm{A}]_e = [\mathrm{A}]_t - [\mathrm{C}]_e \quad \text{and} \quad [\mathrm{B}]_e = [\mathrm{B}]_t - [\mathrm{C}]_e$$

since in the experimental condition, $[B]_t \gg [A]_t$; $[B]_e$ can be equated to $[B]_t$.

The formation constant (*K*) of the complex is

$$K = [C]_e/[A]_e[B]_e \tag{2}$$

Replacing $[B]_e$ by $[B]_t$ and $[A]_e$ as $[A]_t - [C]_e$, we obtain

$$\frac{[A]_t[B]_t}{[C]_e} = \frac{1}{K} + [B]t \tag{3}$$

Taking into consideration that the salts, B, do not contribute to the absorption in the spectral range studied, the total absorbance (OD_t) at any given wavelength is the sum of that due to the complex and the probe. The total OD at any specific wavelength (OD_t) can be expressed as, $OD_t = \epsilon_A[A]_e + \epsilon_C[C]_e$. This can be transformed as $OD_t = \epsilon_A[A]_t + (\epsilon_C - \epsilon_A)[C]_e = OD_A + OD_C$, where OD_A stands for the initial OD due to A at any given wavelength ($= \epsilon_A[A]_t$) and OD_C represents the OD at the same wavelength due to the complex at equilibrium ($= \epsilon_C[C]_e$).

We can write,

$$[\mathrm{C}]_e = \epsilon_A OD_C[A]_t/\epsilon_k OD_A \tag{4}$$

where ϵ_k stands for $(\epsilon_C - \epsilon_A)$.

Substituting the expression for $[C]_e$ from eq 4 into eq 3, we obtain

$$\frac{OD_A}{\mathrm{OD}_t - OD_A} = \frac{1}{[B]_t}\left(\frac{1}{K}\frac{\epsilon_A}{\epsilon_k}\right) + \frac{\epsilon_A}{\epsilon_k} \tag{5}$$

We have employed this equation for the estimation of *K* from the absorption data. According to this equation, a plot of $OD_A/(OD_t - OD_A)$ versus $1/[B]_t$ should yield a straight line whose intercept is given by (ϵ_A/ϵ_k) and the slope ($\epsilon_A/\epsilon_k K$). *K* values were estimated from the slope and the intercept of these plots. Some representative plots based on these equations are shown in Figure 7 and the calculated binding constant values have been collected in Table 3. The fluorescence data have been analyzed based on an equation that can be found elsewhere.[24]

1. Dependence of *K* on the Polarity of the Medium. The data presented in Table 3 can be rationalized as follows: Barring a few scatters, the *K* values are generally higher in toluene compared to the respective values in 1,4-dioxane. This, coupled with the fact that no spectral changes could be observed for these systems in more polar solvents such as acetonitrile or methanol (indicating the instability of the complex), suggests that the complex is charge transfer in nature. Tetraalkylammonium salts exist predominantly as ion pairs in a nonpolar environment and can readily form charge-transfer complexes through electrostatic forces with the dipolar fluorophores. However, in polar media, they exist predominantly as solvated ions and the electrostatic interaction between the solvated cations and the dipolar fluorescent systems is expected to be rather low. Hence, on the basis of these observations, a charge-transfer nature of the 1:1 complex is concluded.

2. Dependence of *K* on the Fluorophore. The *K* values indicate that ANP binds much more strongly with TOAB compared to AP. Moreover, it is pertinent to note in this context that not so dipolar systems (shown in Chart 2) do not display any significant changes in the spectral behavior even in the nonpolar media. Obviously, the dipolar nature of the fluorophore

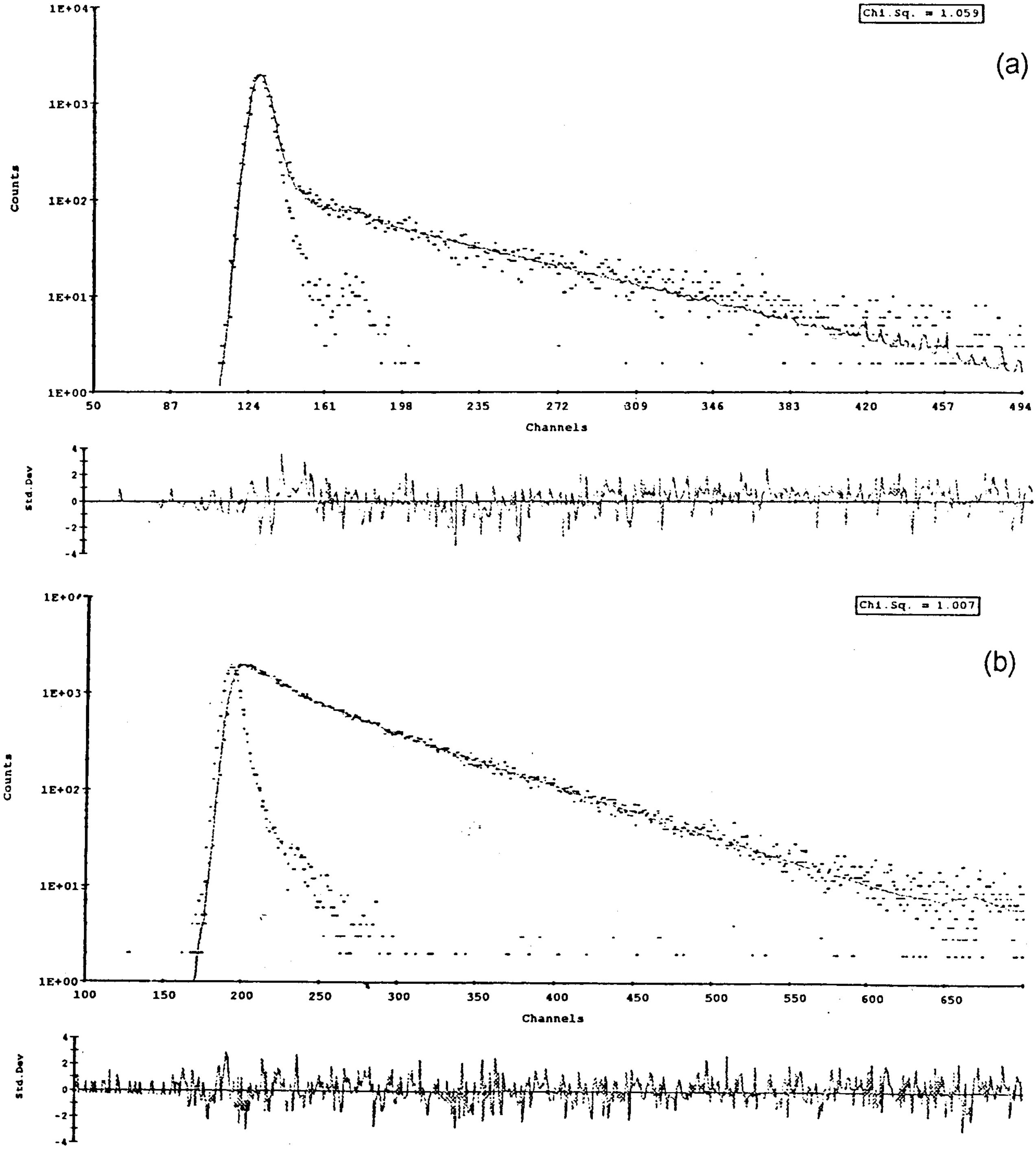

Figure 6. Effect of TOAB on the fluorescence decay behavior of APDEA in the absence (a) and in the presence (b) of TOAB. The monitoring wavelength was 430 and 525 nm for (a) and (b), respectively.

is one of the most important factors that determines the magnitude of the interaction between the fluorophore and the phase-transfer catalyst. A comparatively higher *K* value for ANP is perhaps understandable as the AM1-calculated dipole moments of AP and ANP are 5.3 and 7.5 D, respectively. However, since the interaction between the dipolar fluorophore and the phase-transfer catalyst is governed by electrostatic forces, the absolute values of the charge at the positive and the negative end of the fluorophore and the distance separating them are more more important than their product, dipole moment. When the distance separating the charges is too different for the two fluorophores, one obtains an incorrect assessment of the strength of the interaction from the dipole moment values alone. To avoid this, the mean distance between the 4-amino nitrogen atom and the carbonyl oxygen atom of the fluorophores has been calculated by the AM1 method. The distance is calculated to be 6.1 and 6.8 Å for AP and ANP, respectively. From the values of the dipole moment and the distance, the magnitude of charge localized at the 4-amino nitrogen atom is estimated as 0.18 and 0.23 esu for AP and ANP, respectively. Since the absolute values of the charge (at the positive or negative end of the molecule) is higher for ANP, one can expect a stronger binding compared to AP.

Origin of the New Emission. The fact that the Stokes-shifted new emission band originates from a charge-transfer complex formed between the fluorophore and the phase-transfer catalyst

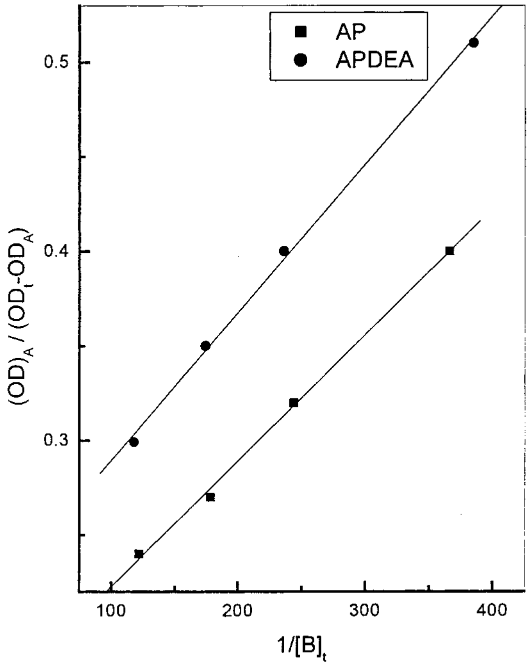

Figure 7. Representative plot of $(OD_A)/(OD_t - OD_A)$ vs $1/[B]_t$ based on eq 5.

Table 3. Binding Constants (in M^{-1}) of TOAB with Various Probe Molecules in Toluene and 1,4-Dioxane As Estimated from the Absorption and the Fluorescence Data.

	binding constants[a]			
	from absorption		from fluorescence	
system	in toluene	in 1,4-dioxane	in toluene	in 1,4-dioxane
AP	175	40	85	105
APDEA	270	90	260	80
ANP	430	110	490	190
ANPDEA	580	230	530	230
NBDEA	110	140	*b*	180

[a] ±10%. [b] Could not be calculated due to the poor quality of the data.

is clearly evident when a comparison is made between the excitation spectra of the systems in the presence and in the absence of tetraalkylammonium salts. Interestingly, the emission maximum of this complex in the presence of tetraalkylammonium salts appears at a longer wavelength, very close to those observed for AP and ANP in a highly polar solvent such as alcohol or water.[24] As the fluorescent band position of the fluorophores is sensitive to the polarity of the medium, one may argue that the tetraalkylammonium salts, especially the chloride, being highly hygroscopic may create a highly polar microenvironment around the fluorophore, which may lead to a Stokes shift of the fluorescence maximums. That fact that a preferential solvation of the fluorophores by the water molecules (associated with the catalysts) is not responsible for the Stokes-shifted new emission band of the systems is evident from the following observations. First, the fluorescence band position observed for the systems in the presence of TBAC is not very different from that observed in the presence of the much less hygroscopic salt, TBOB. Second, we did not observe any change in the absorption/fluorescence maximum of the systems on addition of few drops of water to the toluene solution of AP and ANP. Third, the fluorescence lifetimes of the fluorophores in aqueous or alcoholic solution of the systems are known to be much lower[24] than those observed in the presence of the tetraalkylammonium salts.

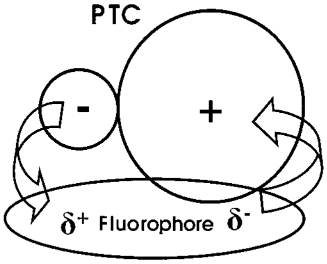

Figure 8. Schematic diagram of the complex indicating enhancement of the charge separation process in the fluorophore induced by the phase-transfer catalyst (PTC).

Role of the Anion. Among the salts employed in this study, the chloride ion is found to be the most effective in inducing the spectral changes. The ability to form the charge-transfer complex under an identical condition is slightly less for the bromide ions. Iodide ion, on the other hand, is found to be rather ineffective, as is the perchlorate ion. This observation, coupled with the fact that only the dipolar fluorophores show changes in the absorption and fluorescence behavior, allows us to understand the exact role of the cationic and the anionic components of the phase-transfer catalyst. In AP and ANP, the positive charge is mainly centered at the 4-amino nitrogen atom and the negative charges are localized on the two carbonyl oxygen atoms. An ion pair, the form in which the phase-transfer catalysts exist in nonpolar media, is most likely to interact with a dipolar system with an antiparallel orientation to form the 1:1 complex. One can therefore propose a structure of the complex as is depicted in Figure 8.

It is to be noted that a Stokes shift of the absorption or fluorescence peak of these dipolar fluorophores can arise due to two factors: a change in the polarity of the immediate environment of the fluorophore and a change in the extent of separation of charge within the fluorophore. The possibility that a change in the polarity of the environment is induced by the phase-transfer catalysts has already been ruled out. This leaves us with only the other choice, an increased separation of charge in the fluorophore. It can be seen that the best way to enhance the charge separation between the 4-amino nitrogen atom and the carbonyl oxygen atoms is when the dipolar fluorophore and the phase-transfer catalyst interact as suggested in Figure 8. The halide ions essentially act as an additional source of electronic charge to the amino nitrogen atom of the fluorophore, and the quaternary ammonium cation by virtue of its location can help the carbonyl oxygen atoms to withdraw more negative charge through the π-conjugated network of the fluorophore. This is how the charge separation in the dipolar fluorophores is enhanced by the salts. The enhancement of the charge separation in the EDA fluorophores by the phase-transfer catalyst as proposed here can be considered to some extent similar to that observed in the presence of the metal salts, as reported previously.[40−43] However, unlike in the previous reports, where the charge separation was primarily controlled by the metal ions, in the present case, the anionic component plays a more important role. This is evident from the data presented in Table 1. Clearly, chloride salts are more effective in enhancing the charge separation in the fluorophore compared to the bromide

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salts. The fact the iodide and perchlorate salts are rather ineffective in this regard can be explained when their sizes are taken into consideration. The charge-to-volume ratio of these anions is much lower than that for the chloride and the bromide salts.

Role of the Cation. The results suggest that the cationic component of the phase-transfer catalyst does not play any significant role in influencing the charge separation process. However, the difference in the fluorescence behavior of the AP and APDEA in the presence of a given PTC can be accounted for by taking into consideration the role of the cation. It has been stated earlier that the intensity of the new Stokes-shifted emission band is significantly higher in the case of APDEA. This shows that the cationic component of the ion pair indeed interacts with the dimethylamino moiety of the three-component system, APDEA, thereby decreasing the through-space photoinduced electron transfer prevalent in the system and increasing the fluorescence intensity of this Stokes-shifted emission. An increase in the fluorescence lifetime of the short-lived species of APDEA in the presence of TOAB corroborates this conclusion.

Excited-State Interaction. The complexation between the phase-transfer catalysts and the fluorophores has been shown to be a ground-state phenomenon. However, it is a matter of interest whether there is an interaction between the two complexing partners in the excited state. Had there been only a ground-state interaction between the two, the fluorescence lifetime would have remained unaffected. However, the fluorescence lifetime data presented in Table 2 show that the lifetime of both AP and ANP is shortened in the presence of TOAB. For example, the fluorescence lifetime of AP in toluene is 13.4 ns in the absence of TOAB. In the presence of 4.4 mM TOAB, the lifetime is lowered to 11.2 ns. Using the Stern−Volmer equation for dynamic quenching,

$$\tau_0/\tau = 1 + k_q\tau_0[\mathrm{TOAB}]$$

(where τ_0 and τ are the fluorescence lifetimes in the absence and presence of TOAB, k_q is the rate constant for the excited-state interaction between the fluorophore and the PTC, and [TOAB] indicates the concentration of TOAB), we obtain a k_q value of 3.3×10^9 M^{-1} s^{-1}. Even though the fluorophore and TOAB interact in the excited state also, one might expect some contribution of this excited-state interaction to the new fluorescence band observed. However, the absence of any growth (negative preexponential factor) in the decay profile of the long-wavelength fluorescence band rules out this possibility.

Conclusion

We have shown in this paper that the quaternary ammonium salts, which are frequently used as phase-transfer catalysts, not only merely solubilize a polar system in a nonpolar medium (thereby enhance the reaction rate) but in the process they can affect the properties of the solubilized systems quite significantly. The results of this investigation clearly demonstrate that a phase-transfer catalyst employed in any investigation cannot be taken as an innocuous reagent that just helps solubilization of a third substance, as is thought commonly. Specifically, from a detailed spectral and time-resolved study on a series of EDA molecules, we have shown how a phase-transfer catalyst binds to a dipolar system in nonpolar media and how this binding changes the photophysical behavior of the systems. It is shown that the influence of a phase-transfer catalyst in modifying the properties of a system depends to a large extent on the dipolar nature of the fluorescent systems. Moreover, the anionic part of the ion pair, the form in which the phase-transfer catalysts exist in nonpolar media, seems to influence the photophysical properties of the EDA systems much more than the cationic counterpart.

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