Influence of phase transfer catalysts on the photophysical properties of electron donor-acceptor molecules

The steady state and time-resolved fluorescence behavior of several electron donor acceptor (EDA) molecules in nonpolar media containing tetraalkylammonium salts, which are used extensively in chemical applications as phase transfer catalysts (PTCs), are described in this chapter.

3.1. Introduction

Tetraalkylammonium halides with one or two large alkyl groups, such as cetyltrimethyl ammonium bromide (CTAB), are known as good surfactants. These substances 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) or large ones (e.g. tetraoctylammonium halides) with all four identical alkyl groups 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. In a binary two-phase solution, a good phase transfer catalyst circulates between the two phases across the interface instead of staying in a single phase like micelles. These PTCs are generally less stable in aqueous medium. In nonpolar media, these are highly
soluble and known to exist as ion pairs.\textsuperscript{1,2} Interestingly, even though the utility of the phase transfer catalysts in synthetic chemistry is rather well documented,\textsuperscript{1,3-5} not much attention has been paid to understand the exact nature of the binding of these salts with polar organic molecules in a nonpolar medium. Recently PTCs have been effectively used to stabilize nanoparticles in a nonpolar medium.\textsuperscript{14-16} Here we address ourselves to a fundamental question of finding out whether the role of the phase transfer catalysts lies merely helping the solubilization of a polar system in nonpolar media so as 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. In order to achieve this objective, we have selected several fluorescent electron donor-acceptor (EDA) systems as the probe molecules. Since the absorption and fluorescence behavior of these systems is mainly controlled by a low-lying intramolecular charge transfer (ICT) state, whose location is extremely sensitive to the surrounding medium, it is expected that the changes in the absorption and fluorescence properties induced by the PTCs will provide information on how the ion pairs interact with the probe molecules. The chosen EDA molecules can be categorized in two sets (Fig. 3.1). Set 1 consists of 4-aminophthalimide (AP) and 4-aminonaphthalimide (ANP), both known as highly fluorescing EDA molecules especially in nonpolar media. Both the molecules exhibit a broad emission band that originates from an ICT state, with the fluorescence parameters strongly dependent on the polarity of the media.\textsuperscript{17-23} In Set 2, three multi-component systems, APDEA, ANPDEA and NBDEA with a
fluorophore-spacer-receptor architecture have been chosen. The first two systems, APDEA and ANPDEA contain AP and ANP as the fluorophore linked with a dimethylamino group (as receptor for cations) via a dimethylene spacer.\textsuperscript{21} NBDEA is another similar system containing a dimethylamino-nitrobenzoxadiazole (NBD) moiety, a popular fluorescence probe in biological
The solvent sensitive fluorescence properties of the NBD derivatives and the ability of NBDEA in sensing various metal ions are well documented. The fundamental difference in the photophysical properties of the parent systems (shown in set 1) and the multi-component systems (set 2) is that the former set of molecules are highly fluorescent (at least in the nonpolar media) while the latter are not. The low fluorescence quantum yields of the three-component systems are due to through-space photoinduced intramolecular electron transfer (PIET) between the receptor and fluorophore moieties. PIET leads to 'switching off' of the fluorescence. However, in the presence of a guest capable of tying up the lone pair of electrons of the receptor, PIET communication between the receptor and the fluorophore gets cut-

**Set 3**

![Chemical structures](image)

**Fig. 3.2**
off and the fluorescence of the system is 'switched on'.\textsuperscript{17,21,27,28} We have also examined the effect of tetraalkylammonium salts on a few other systems (MNP and NP) that do not contain the strong electron donating amino group at the 4-position and NPDEA, which comprises NP as the fluorophore but contains an additional site for the cation binding. These systems are shown as Set 3 in Fig. 3.2. We thought that a study of the effect of the PTCs on the photophysical behavior of these systems would help understanding the exact role of the PTCs and in obtaining an answer to the question raised above.

\textbf{3.2. Spectral properties}

\textbf{3.2.1. Absorption spectra}

The effect of TOAB on the UV-visible absorption spectrum of AP is illustrated in Fig. 3.3 (a). With progressive addition of TOAB the long-wavelength charge transfer band of AP, which shows a maximum at around 350 nm in toluene, shifts towards red with a gain in intensity in the longer wavelength region. The presence of an isosbestic point at around 350 nm clearly suggests 1:1 complexation between AP and TOAB. In the presence of 4.4 mM TOAB the observed red shift in the absorption maximum of AP is \(\sim\) 20 nm. A similar observation has been made in the presence of TBAB and TBAC, where the observed spectral shift are \(\sim\)12 nm and \(\sim\)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 [Fig. 3.3 (b)]. The spectral data of this system in the presence and in absence of various phase transfer catalysts are given in Table 3.1.
Fig. 3.3. Effect of TOAB on the UV-visible absorption behavior of (a) AP and (b) APDEA in toluene. The concentrations of TOAB in increasing order of the absorbance at the longest wavelength maxima were 0, 0.66, 1.46, 2.19 and 4.39 mM in (a) and 0, 0.37, 0.66, 1.39, 2.27 and 4.54 mM in (b) respectively.
Fig. 3.4. Effect of TOAB on the UV-visible absorption behavior of (a) ANP and (b) ANPDEA in toluene. The salt concentrations in increasing order of the absorbance at the longest wavelength maxima were 0, 0.15, 0.44, 0.88 and 1.54 mM in (a) and 0, 0.29, 0.88, 1.09, 1.83 and 3.73 mM in (b) respectively.
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 has been observed. The absorption behavior of ANP and ANPDEA in the presence of the TOAB (depicted in Fig. 3.4) also indicates 1:1 complexation between these systems and TOAB. The spectral data for these systems in the presence of other phase transfer catalysts are also represented in Table 3.1.

Table 3.1. *Absorption and fluorescence spectral maxima observed for various systems in toluene in the presence of different tetraalkylammonium salts.*

<table>
<thead>
<tr>
<th>System</th>
<th>None</th>
<th>TOAB</th>
<th>TBAB</th>
<th>TBAC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{abs}}^{\text{max}}$ (nm)</td>
<td>$\lambda_{\text{flu}}^{\text{max}}$ (nm)</td>
<td>$\lambda_{\text{abs}}^{\text{max}}$ (nm)</td>
<td>$\lambda_{\text{flu}}^{\text{max}}$ (nm)</td>
</tr>
<tr>
<td>AP</td>
<td>350</td>
<td>430</td>
<td>370</td>
<td>467</td>
</tr>
<tr>
<td>APDEA</td>
<td>353</td>
<td>430</td>
<td>379</td>
<td>502</td>
</tr>
<tr>
<td>ANP</td>
<td>403</td>
<td>469</td>
<td>420</td>
<td>520</td>
</tr>
<tr>
<td>ANPDEA</td>
<td>403</td>
<td>470</td>
<td>436</td>
<td>522</td>
</tr>
<tr>
<td>NBDEA</td>
<td>445</td>
<td>517</td>
<td>455</td>
<td>525</td>
</tr>
<tr>
<td>NPDEA</td>
<td>345, 370,</td>
<td>345, 370,</td>
<td>345, 370,</td>
<td>345, 370,</td>
</tr>
<tr>
<td></td>
<td>332</td>
<td>397</td>
<td>332</td>
<td>332</td>
</tr>
</tbody>
</table>

$^a$~$2 \times 10^{-5}$ M solution of the compounds in toluene was used at room temperature; the concentration of the PTCs was ~ 1.7 mM in the case of TBAC and 4.4 mM for the other salts; $\lambda_{\text{ex}}$ = 350 nm for AP, APDEA, 305 nm for NPDEA, 380 nm for ANP, ANPDEA and 415 nm for NBDEA.
NBDEA too exhibits a Stokes shift of the absorption maximum in the presence of the tetraalkylammonium salts and the magnitude of the shift lies between 12 - 25 nm (vide Table 3.1). In this case, even though 1:1 complexation is indicated for lower concentration of TOAB, higher order complexes could be observed (as evident from the loss of isosbestic point) at higher concentration of the salt.

The other observations can be summarized as follows: Even though spectral changes similar to what have been described above could be observed for all the systems shown in Fig. 3.1 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 \( (E_r(30) = 36.0) \), which is slightly more polar than toluene \( (E_r(30) = 33.9) \), the complexation could be observed though not as prominently as in the case of toluene. This is illustrated in Fig. 3.5. Moreover, in this solvent, very often the initial isosbestic point could not be seen for higher concentration of the salts. Secondly, none of the systems exhibit any significant changes in the spectral behavior (even in nonpolar media) with PTCs such as TBAI or TBAP. Thirdly, for systems such as NP, MNP, which do not contain the amino group at the 4-position of the naphthalimide ring, no spectral changes could be observed with the tetraalkylammonium salts employed in this study. Moreover, it was found that NPDEA, which contains a cation-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.
3.2.2. Fluorescence spectra

In toluene, AP exhibits a broad structureless fluorescence band with a maximum at around 430 nm. In the presence of PTCs, this fluorescence gets quenched and a relatively weak new emission band appears at a longer wavelength (Fig. 3.6). 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 presence of ~1.7 mM TOAB, TBAB, and TBAC are observed at 475, 503, and 520 nm, respectively (vide Table 3.1). While a similar behavior is noticed in the case of ANP (Fig. 3.6), the multi-component systems (APDEA, ANPDEA and NBDEA) behave slightly differently.
Fig. 3.6. Effect of TOAB on the fluorescence behavior of (a) AP and (b) ANP in toluene. TOAB concentrations were 0, 0.51, 1.02 and 1.46 mM in (a) and 0, 0.15, 0.44, 0.88, 1.54 and 1.98 mM in (b) respectively. The excitation wavelength was 335 nm for AP and 380 nm for ANP.
For the latter systems, in the presence of PTCs the original fluorescence gets quench and simultaneously a new emission band comes up at longer wavelength region. The new fluorescence band is found to be drastically Stokes-shifted relative to the original fluorescence maximum (Fig. 3.7). The degree of enhancement of the fluorescence intensity relative to the original fluorescence band is found to be as large as 25-fold in case of APDEA. The changes in the fluorescence behavior of the molecules (set 1 and 2 in Fig. 3.1) as stated above could also be observed in other nonpolar solvents such as cyclohexane ($E_T(30) = 30.9$). In 1,4-dioxane ($E_T(30) = 36.0$), which is slightly more polar, the new emission is found to be much weaker compared to that observed in toluene ($E_T(30) = 33.9$). The spectral data of the systems in 1,4-dioxane in the presence of TOAB are given in Table 3.2. Fig. 3.8 shows the influence of TOAB on the fluorescence behavior of ANPDEA in 1,4-dioxane. 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 has been observed even in nonpolar environment. TBAI and TBAP are found to have no significant influence on the fluorescence behavior of these systems even in the nonpolar media.
Fig. 3.7. Effect of TOAB on the fluorescence behavior of (a) APDEA and (b) ANPDEA in toluene. TOAB concentrations were 0, 0.37, 0.66, 1.39, 2.27, 3.07 and 4.54 mM in (a) and 0, 0.29, 0.88, 1.09, 1.46 and 1.83 mM in (b). APDEA and ANPDEA were excited at 345 nm and 380 nm respectively.
Table 3.2. Absorption and fluorescence spectral maxima observed for various systems in 1,4-dioxane in the presence of tetraoctylammonium bromide (TOAB). \(^a\)

<table>
<thead>
<tr>
<th>Systems</th>
<th>(\lambda_{\text{abs}}^{\text{max}}) (nm)</th>
<th>(\lambda_{\text{flu}}^{\text{max}}) (nm)</th>
<th>(\lambda_{\text{abs}}^{\text{max}}) (nm)</th>
<th>(\lambda_{\text{flu}}^{\text{max}}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP</td>
<td>355</td>
<td>437</td>
<td>360</td>
<td>450</td>
</tr>
<tr>
<td>APDEA</td>
<td>360</td>
<td>449</td>
<td>365</td>
<td>474</td>
</tr>
<tr>
<td>ANP</td>
<td>409</td>
<td>503</td>
<td>424</td>
<td>514</td>
</tr>
<tr>
<td>ANPDEA</td>
<td>410</td>
<td>477, 503</td>
<td>425</td>
<td>518</td>
</tr>
<tr>
<td>NBDEA</td>
<td>450</td>
<td>528</td>
<td>460</td>
<td>543</td>
</tr>
</tbody>
</table>

\(^a\)~2 \times 10^{-5}\ M solution of the compounds in 1,4-dioxane was used at room temperature; Concentration of the TOAB was \(\sim 7.5\) mM for NBDEA and \(\sim 6.7\) mM for others; \(\lambda_{\text{ex}} = 370\) nm for AP, 355 nm APDEA, 410 nm for ANP, 415 nm for ANPDEA and 460 nm for NBDEA.

Fig. 3.8. Effect of TOAB on the fluorescence behavior of ANPDEA in 1,4-dioxane. TOAB concentration was 0, 1.2, 2.6 and 6.9 mM respectively. The sample was excited at 415 nm.
3.2.3. Fluorescence excitation spectra

In order to identify the origin of the new fluorescence emission we have measured fluorescence excitation spectra for all the systems monitoring the original fluorescence as well as the Stokes-shifted fluorescence band. A typical fluorescence excitation spectrum of AP in toluene is shown in Fig. 3.9. 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.

![Fluorescence excitation spectra](image)

**Fig. 3.9.** Effect of TOAB on the fluorescence excitation spectra of AP in toluene. TOAB concentration was 0 in (i) and 4.39 mM in (ii). The monitoring wavelengths were 430 and 467 nm respectively.
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 quaternary ammonium salts. This suggests that the new emission originates from the ground state complex formed between the salts and the probe molecules.

3.2.4. Fluorescence decay behavior

With a view to obtaining further details on the nature of the interaction between the PTCs and fluorophores, we have also investigated the fluorescence decay behavior of the present systems in the absence and presence of the salts. In the presence of PTCs, we have measured the decay curves 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 3.3. Some representative decay profiles depicting the influence of PTC along with the best fit to the decay are shown in Fig. 3.10. and Fig. 3.11. The main features of the decay behavior can be summarized as follows:

The major component of AP has a lifetime between 13 - 17 ns in toluene and 1,4-dioxane. In the presence of 4.4 mM TOAB, the $\tau$ 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.
Table 3.3. Fluorescence decay parameters\(^a\) for the systems studied in the absence and in presence of TOAB (\textasciitilde 4 mM) in toluene and 1,4-dioxane.

<table>
<thead>
<tr>
<th>Fluorophore</th>
<th>Solvent</th>
<th>Lifetimes/ns without TOAB</th>
<th>Lifetimes/ns in presence of TOAB</th>
<th>at short w.l.(^b)</th>
<th>at long w.l.(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AP</td>
<td>toluene</td>
<td>3.9 (0.03)</td>
<td>2.7 (0.06)</td>
<td>3.2 (0.03)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,4-dioxane</td>
<td>13.4 (0.08)</td>
<td>11.2 (0.06)</td>
<td>12.2 (0.09)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>16.9 (0.07)</td>
<td>1.5 (0.03)</td>
<td>13.5 (0.08)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>APDEA</td>
<td>toluene</td>
<td>0.1 (5.75)</td>
<td>0.5 (0.35)</td>
<td>2.9 (0.07)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,4-dioxane</td>
<td>13.3 (0.01)</td>
<td>9.4 (0.02)</td>
<td>12.8 (0.05)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2 (1.84)</td>
<td>0.7 (0.22)</td>
<td>2.7 (0.08)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>17.5 (0.004)</td>
<td>12.0 (0.04)</td>
<td>13.1 (0.04)</td>
<td></td>
</tr>
<tr>
<td>ANP</td>
<td>toluene</td>
<td>1.6 (0.06)</td>
<td>1.9 (0.13)</td>
<td>8.5 (0.11)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,4-dioxane</td>
<td>8.8 (0.08)</td>
<td>8.3 (0.03)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>11.1 (0.11)</td>
<td>9.0 (0.11)</td>
<td>9.9 (0.11)</td>
<td></td>
</tr>
<tr>
<td>ANPDEA</td>
<td>toluene</td>
<td>2.1 (0.17)</td>
<td>1.9 (0.17)</td>
<td>1.9 (0.07)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,4-dioxane</td>
<td>3.3 (0.12)</td>
<td>4.4 (0.01)</td>
<td>8.1 (0.06)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.3 (0.03)</td>
<td>2.3 (0.09)</td>
<td>3.1 (0.06)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.1 (0.05)</td>
<td>8.6 (0.08)</td>
<td></td>
</tr>
<tr>
<td>NBDEA</td>
<td>toluene</td>
<td>0.3 (0.91)</td>
<td>0.3 (0.79)</td>
<td>0.3 (0.61)</td>
<td></td>
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<tr>
<td></td>
<td>1,4-dioxane</td>
<td>6.4 (0.01)</td>
<td>6.7 (0.01)</td>
<td>7.1 (0.01)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2 (1.56)</td>
<td>0.6 (0.36)</td>
<td>1.2 (0.19)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.2 (0.03)</td>
<td>5.3 (0.01)</td>
<td>14.7 (0.02)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Decay curves were fitted to a single or biexponential function depending on the quality of the plot of the residuals and the \(\chi^2\) values; preexponential factors were shown within the brackets; \(^b\)short wavelength corresponds to 400, 450, and 495 nm for AP, ANP and NBD derivatives and long wavelength corresponds to 480, 540 and 555 nm respectively.
Fig. 3.10. Effect of TOAB on the fluorescence decay behavior of APDEA in toluene (a) in the absence and (b) in the presence of TOAB. The monitoring wavelength was 430 nm and 525 nm for (a) and (b) respectively. \( \lambda_{ex} \) was 340 nm in both cases.
Fig. 3.11. Effect of TOAB on the fluorescence decay behavior of NBDEA in 1,4-dioxane (a) in the absence and (b) in the presence of TOAB. The monitoring wavelength was 530 nm and 550 nm for (a) and (b) respectively. $\lambda_{ex}$ was 450 nm in both cases.
In contrast to AP, the major component of the decay in the case of the 3-component system, APDEA is a very short-lived species. This is due to the photoinduced intramolecular electron transfer (PIET) quenching of the fluorescence. On addition of TOAB, an increase in the \( \tau \) values of the short-lived component could be observed. Since in the case of ANPDEA, PIET is not very significant, 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 \( \tau \) values of the major component of the decay is not very significant, as can be seen from Fig. 3.11.

### 3.3. Discussion

#### 3.3.1. Formation constant (K) of the complexes

The phase transfer catalysts induced changes in the absorption behavior of the systems indicate the formation of a 1:1 complex in the ground state in nonpolar media. The formation constants of the complexes have been evaluated from the absorption data using the equation 3.1 (derivation of the equation is given in appendix 1). Considering 1:1 complexation between the probe molecule, A and the phase transfer catalyst, B, the complexation process can be simply written as

\[
A + B \leftrightarrow C
\]

where, C stands for the complex. The final expression used for estimation of the binding constant is as follows:

\[
\frac{OD_A}{OD_t - OD_A} = \frac{1}{[B]_t} \left( \frac{1}{K \varepsilon_k} \right) + \frac{\varepsilon_A}{\varepsilon_k} \tag{3.1}
\]
where, $OD_A$ stands for the initial optical density of A at given wavelength ($\lambda$), $(OD_t)$ is the total absorbance at the same $\lambda$ in the presence of PTC at a concentration of $[B]_t$. According to equation 3.1, a plot of $OD_A/(OD_t - OD_A)$ vs $1/[B]_t$ should yield a straight line whose intercept is given by $(\varepsilon_A/\varepsilon_k)$ and the slope $(\varepsilon_A/\varepsilon_k K)$. K values were estimated from the slope and the intercept of these plots. Some representative plots based on these
equations are shown in Fig. 3.12 and the calculated binding constant values have been collected in Table 3.4.

![Graph with data points and a straight line](image)

**Fig. 3.13** Representative plot of $\phi_A / (\phi - \phi_A)$ vs $1/[B]_t$, based on equation 3.2. The data points denote for AP (H), APDEA (σ) and ANPDEA (υ) in toluene respectively and the straight line represent the best fit to the data.

We have further estimated the binding constant from steady state fluorescence intensity data according to equation 3.2 (derivation of this equation is provided in appendix 1).  

$$\frac{\phi_A}{\phi - \phi_A} = \left[ \left( \frac{\phi_A}{\phi_C - \phi_A} \right) \frac{1}{K} \frac{1}{[B]_t} + \frac{\phi_A}{\phi_C - \phi_A} \right]$$  

(3.2)
In this equation, $\phi$ and $\phi_A$ are the emission intensities in presence and absence of PTC at a particular wavelength where the effect of complexation is prominent. In Fig. 3.13, the linear fits to the data points of AP, APDEA and ANPDEA in toluene, obtained using equation 3.2 are shown. The calculated binding constant values using equation 3.2 are given in Table 3.4.

**Table 3.4.** Binding constant of TOAB with various probe molecules in toluene and 1,4-dioxane estimated from the absorption and the fluorescence data.

<table>
<thead>
<tr>
<th>System</th>
<th>Binding constant$^a$/ M$^{-1}$</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>from absorption</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>toluene</td>
<td>1,4-dioxane</td>
<td>toluene</td>
<td>1,4-dioxane</td>
<td></td>
</tr>
<tr>
<td>AP</td>
<td>175</td>
<td>40</td>
<td>85</td>
<td>105</td>
<td></td>
</tr>
<tr>
<td>APDEA</td>
<td>270</td>
<td>90</td>
<td>260</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>ANP</td>
<td>430</td>
<td>110</td>
<td>490</td>
<td>190</td>
<td></td>
</tr>
<tr>
<td>ANPDEA</td>
<td>580</td>
<td>230</td>
<td>530</td>
<td>230</td>
<td></td>
</tr>
<tr>
<td>NBDEA</td>
<td>110</td>
<td>140</td>
<td>b</td>
<td>180</td>
<td></td>
</tr>
</tbody>
</table>

$^a \pm 10\%$; $^b$ could not be calculated due to the poor quality of the data.

The data presented in Table 3.4 can be rationalized as follows: Barring a few scatter, 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-pair in nonpolar environment and can readily form charge transfer complex through electrostatic forces with the dipolar fluorophores. However, in the 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, based on these observations, a charge transfer nature of the 1:1 complex is concluded.

Between AP and ANP, the K values are relatively higher for the latter indicating a stronger binding of TOAB with ANP compared to AP. A similar trend is also noticed in case of APDEA and ANPDEA. Moreover, it should be noted that the dipolar systems (shown in set 3 Fig 3.2) do not display any significant changes in the spectral behavior even in the nonpolar media. Obviously, the dipolar nature of the fluorophore is one of the most important factors that determine 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 (Austin model 1) 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 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. In order to avoid this, the mean distance between the 4-amino nitrogen atom and the carbonyl oxygen atom of the fluorophores has been calculated by AM1
method. The estimated distance is 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) are higher for ANP, one can expect a stronger binding compared to AP.

3.3.2. 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 is clearly evident when a comparison is made between the excitation spectra of the systems in the presence and in 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. As the fluorescence band position of the fluorophores is sensitive to the polarity of the medium, it may possible that the tetraalkylammonium salts, especially the chloride, being highly hygroscopic create a highly polar microenvironment around the fluorophore, which may lead to a Stokes shift of the fluorescence maxima. The 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 are not very different from that observed in the presence of much less...
hygroscopic salt, TBOB. Second, we have not observed 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\textsuperscript{30} than those observed in the presence of the tetraalkylammonium salts. All these observations clearly rule out the possibility of a change in polarity of the microenvironment around the dipolar probe molecules in the presence of PTCs.

### 3.3.3. Role of anion and cation

Our spectroscopic data indicate a highest efficiency of the chloride ion in inducing the spectral changes compared to other anions. The ability to form the charge transfer complex under an identical condition is slightly less for the bromide ions. On the other hand, iodide and perchlorate ions are found to be rather ineffective in such a complex formation process. 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 anti-parallel orientation to form the 1:1 complex. One can therefore propose a structure of the complex as is depicted in Fig. 3.14.
Fig. 3.14. *A schematic diagram of the complex indicating enhancement of the charge separation process in the fluorophore induced by the phase transfer catalyst (PTC).*

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 Fig. 3.14. 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 quaternary 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 presence of the metal salts. 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. That is evident from the spectral data presented in Table 3.1. Clearly, chloride salts are more effective in enhancing the charge separation in the fluorophore compared to the bromide salts. The fact that iodide and perchlorate salts are rather ineffective in this regard can be explained when one can considers their size. A large size of these anions implies a low charge to volume ratio and less effectiveness in stabilizing a positive centre.

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 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.
3.3.4. *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 also. 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 3.3 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,

$$\frac{\tau_0}{\tau} = 1 + k_q \tau_0 [TOAB]$$  \hspace{1cm} (3.3)

where, $\tau_0$ and $\tau$ 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 obtained a $k_q$ value of $3.3 \times 10^9$ 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.

3.4. *Conclusion*

In this chapter from a detailed steady state and time resolved studies on several dipolar probe molecules, we have shown 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 can not 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.

3.5. References

(1) Dehmlow, E. V.; Dehmlow, S. S. Phase Transfer Catalysis; Verlag Chemie: Weinheim, 1983.


