4N,N-DIMETHYLAMINOPHTHALIMIDE AND ITS FATTY ACID DERIVATIVE AS SENSORS IN MICELLAR MEDIA.

The fluorescence behaviour of 4-N,N-dimethylaminophthalimide (DAP, Chart 5.1) and its fatty acid derivative, 11-(4-N,N-dimethylaminophthalimido)undecanoic acid (DAPL, Chart 5.1) in micellar media is described in this chapter. The aim of this investigation is to find out the potential of these compounds as fluorescence probes for characterising the organised environments.

5.1. Introduction

The elegant usage of the fluorescent EDA molecules in probing the microstructures of various organised media, is well documented. In the
previous chapter, such usage is illustrated with EDA molecules, AP and its derivative, APL. A new class of fluorescence probes, which show remarkably higher sensitivity toward solvent polarity are systems, where the electron donor and the acceptor moieties are formally linked by a single bond. On excitation, this class of systems often display an additional charge transfer emission band which is believed to originate from a state (called TICT state) in which the donor and acceptor moieties are perpendicular to each other. The fluorescence originating from such a state is much more sensitive to the solvent polarity due to the large dipolar character of the TICT state resulting from complete decoupling of the donor and acceptor orbitals with one unit of charge transfer. In some EDA systems, the TICT state is well-above the locally excited ICT state or the barrier to ICT→TICT process is sufficiently large so that the TICT does not influence the Photophysical behaviour of the systems. AP can be considered as one such systems. In many systems, TICT can be nonfluorescent. The presence of a low-lying TICT state, whether emitting or not, enhances the sensitivity of the fluorescent properties of the locally excited ICT state because of the polarity dependence of the nonradiative ICT→TICT process. The best known examples of such systems are coumarin dyes. The highly sensitive fluorescence properties of the coumarins have been explained due to the presence of low-lying nonfluorescent TICT state and this has been exploited extensively to probe the micropolarity of the organised systems and to study the solvent relaxation processes.
Recently, a comparative study of the Photophysical behaviour AP and DAP has revealed that the fluorescence properties of DAP are much more sensitive to the solvent polarity compared to AP.\textsuperscript{14} This observation is attributed to the presence of a nonfluorescent TICT state below the locally excited emitting state of DAP and also due to the enhanced dipole moment of its fluorescent state.\textsuperscript{14} Therefore, one expects, that the fluorophores based on DAP to be superior to those based on AP. In addition, the dimethyl substitution of the amino hydrogens of AP is expected to enhance the hydrophobicity of the fluorophore which might help its deeper penetration into the core region of the micelle. With this view in mind we have explored the potential of DAP and DAPL as fluorescence probes in micellar media.

DAP exhibits a shift of $\approx$120 nm on changing the solvent from 1,4-dioxane to water.\textsuperscript{14} The fluorescence quantum yield ($\phi_f$) decreases by a factor of $\approx$620 for the same change of solvent. In aprotic media, when the solvent changes from 1,4-dioxane to acetonitrile, the $\phi_f$ decreases by a factor of $\approx$5 and the nonradiative rate constant ($k_{nr}$) increases by a factor of $\approx$10.\textsuperscript{14} On the other hand, the fluorescence yield, lifetime and $k_{nr}$ values remain more or less same in these solvents for AP. This disparity in the fluorescence behaviour of DAP when compared to that for AP, is attributed to the presence of a nonradiative decay channel (nonfluorescent TICT state) even though the emission in both cases originates from the ICT state. Clearly, the change in the fluorescence yields with variation of solvents, which is an indicator of the
effectiveness of a probe, is much higher for DAP than that of AP.\textsuperscript{14} All these observations suggest that DAP can act as a more efficient probe than AP. We have therefore undertaken the following investigation employing DAP and its derivatives in three types of surfactants, cationic (CTAB), anionic (SDS), and neutral (TX).\textsuperscript{15}

5.2. **DAP as a Sensor for Micellar Media**

5.2.1. *Absorption Spectra*

Fig. 5.1 shows the absorption spectra of DAP in the presence of CTAB surfactant. The changes in the spectra on addition of the surfactant are rather small. A very similar behaviour is observed with SDS and TX. This observation is in accordance with the results obtained with AP and APL.

5.2.2. *Fluorescence Spectra*

Addition of surfactants to an *aq* solution of DAP has marked effect on its fluorescence behaviour. Fig. 5.1 displays the fluorescence spectra of DAP as a function of CTAB concentration. A blue-shift of the spectral maximum and an enhancement of the fluorescence intensity are the two noticeable observations that can be made on addition of CTAB to an *aq* solution of DAP. The change in the fluorescence properties is significant only beyond a certain concentration of the surfactant. The blue-shift of the spectra and increase in the fluorescence yield are clearly due to as the binding of the probe to a less polar site of the micellar environment than the bulk *aq* phase once the micelles are formed. The
Fig. 5.1. Absorption (a) and fluorescence (b) spectra of DAP in aqueous solution with different amounts of CTAB. The concentrations of CTAB (mM) (a) for the spectra labelled 1-5 are 0, 6, 12, 30, and 71 respectively; (b) in increasing order of intensity, 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2, 2.5, 6.3, 10, 15, 21, 28, 33, 39, 62, 71, respectively. $\lambda_{\text{exc}} = 410$ nm.
decrease in the polarity of the microenvironment of the probe leads to greater destabilisation of the emitting state compared to the ground state (as the excited state dipole moment of DAP is higher than the ground state moment). This results in an increased separation between the SQ and $S_1$ states which lowers the nonradiative transition rate from $S_1$ leading to an increase in the fluorescence yield. The reduction in hydrogen bonding interaction with the solvent could also be responsible for an increase in the fluorescence yield on micellisation. The behaviour of DAP in cationic (SDS) and neutral (TX) micelles is found to be quite similar.

The maximum spectral shift and the fluorescence enhancement data in three micelles are gathered in Table 5.1. A quantitative analysis of the fluorescence enhancement data gave the CMC values of the surfactants employed (Fig. 5.2). The insert in Fig. 5.2 shows the variation of the $f_{c}/f_{o}$ with the surfactant concentration over the entire range used. From the inflection point of the two straight lines in the Fig. 5.2, the CMC of the CTAB is estimated to be $(0.6 \pm 0.03) \times 10^{-3}$ M. Similarly, the estimated CMC values of SDS and TX are found to be $(7.8 \pm 0.4) \times 10^{-3}$ M and $(0.26 \pm 0.02) \times 10^{-3}$ M, respectively. A fairly good agreement of the measured CMC values with the literature can be found from Table 5.1. The important point that is to be noted here is that the change in the relative fluorescence intensity and shift in the emission maximum (Table 5.1) for DAP are considerably higher in micellar
media when compared to those for AP. This makes DAP clearly more efficient than AP in monitoring even subtle changes in the surrounding environment.

Fig. 5.2. A plot of the relative fluorescence intensity ($\phi_f/\phi_0$) of DAP as a function of CTAB concentration in aqueous solution. The insert shows the variation of the ratio over a larger concentration range.

[CTAB] x $10^3$ M

Fig. 5.2. A plot of the relative fluorescence intensity ($\phi_f/\phi_0$) of DAP as a function of CTAB concentration in aqueous solution. The insert shows the variation of the ratio over a larger concentration range.
Table 5.1: Fluorescence Enhancement, Spectral Shift and Lifetime of DAP in Micellar Media along with the Binding Constants.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Concentration (mM)</th>
<th>CMC (mM)</th>
<th>( \Phi_i/\Phi_0 )</th>
<th>Shift (nm)</th>
<th>( \tau_i ) (ns)</th>
<th>( K ) (M(^{-1}))</th>
<th>Literature Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS</td>
<td>75</td>
<td>8.00</td>
<td>7.1</td>
<td>30</td>
<td>0.52</td>
<td>11600</td>
<td>(98.7)</td>
</tr>
<tr>
<td>CTAB</td>
<td>72</td>
<td>41</td>
<td>8.8</td>
<td>41</td>
<td>0.92</td>
<td>11850</td>
<td>(98.8)</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>139</td>
<td>53</td>
<td>20.7</td>
<td>53</td>
<td>0.26</td>
<td>21400</td>
<td>(96.7)</td>
</tr>
</tbody>
</table>

\( a \) From ref. [1]. \( b \) Calculated using relative amplitude, \( R_i = 100 \Phi_i/\Phi_0 \).
5.2.3. Time-resolved Measurements

The fluorescence lifetimes of DAP have been measured by selecting the surfactant concentrations such that most of the probe molecules are micellised. The lifetime data in micellar media are shown in Table 5.1 which has been obtained from a biexponential fit of the fluorescence decay curves in the respective media. The lifetime of the major species (97-99%) ranges between 0.3-0.8 ns which is considered as the lifetime of the micellised probe. This lifetime is 2-5 folds higher than that of DAP in aq medium (~ 0.18 ns). Though the enhancement of lifetime of DAP on micellisation is very clear from the data, it is not possible to quantify the lifetime enhancement data because the time-resolution of our instrument (1.4 ns) is considerably lower than the lifetimes measured both in aq and micellar media.

5.2.4. Binding Strength of DAP with Micelles

Binding constants (K) of DAP with the micelles have been determined by following the method described earlier (equation 3.3). The plot based on this equation is shown in Fig. 5.3 from which the K values (± 10%) are evaluated as 11600, 11850 and 21400 M⁻¹ in SDS, CTAB and TX, respectively. The measured K values are consistent with the spectral shift data. Compared to the binding of AP with the micelles, DAP binds relatively strongly (K values are higher by a factor of 3.4 - 3.8) which could be most likely due to the hydrophobic influence of the methyl groups.
5.2.5. Location of DA P in Micelles

With DAP, the observed enhancement of fluorescence intensity in micellar environment is 7-21 fold, whereas the expected enhancement for a 1,4-dioxane like environment is nearly 600 fold. Quite obviously, DAP experiences an environment that is considerably polar. However, the polarity experienced by DAP is less polar than water. One arrives at a similar conclusion on
consideration of the spectral shift data. The microscopic polarities (in ET(30)\textsuperscript{16} scale) for the solubilization sites of DAP, by following the method described in
the previous chapter, are 57.3, 55.1 and 52.8 in SDS, CTAB and TX, respectively. The interface polarities as estimated by DAP are not very different
from those estimated by AP. The slightly lower polarity estimates obtained with DAP are presumably due to a slightly deeper penetration of this probe towards
the core region compared to AP.

One of the findings that is common in both cases is that the interface in
SDS micelle is relatively more polar than in CTAB and TX. This is in
accordance with the observation of Menger and co-workers who proposed the
SDS micellar aggregates to have a large wet Stern region, and a rough
surface.\textsuperscript{17} There were also supportive reports for the more porous nature and
'wet' micelles of SDS from small angle neutron scattering (SANS) studies.\textsuperscript{18} On
the other hand, SANS data on CTAB micelles excluded the possibility of wet
and rough surfaces.\textsuperscript{18a,19} Recently, Sarpal et al\textsuperscript{20} have also provided the
evidence for surface roughness of SDS micelles by employing 3H-indole
derivatives as fluorophores. The irregularities caused by the surface roughness
are probably filled by the water molecules. The more porous nature or high
surface roughness of SDS micelles is probably the reason for higher polarity
sensed by DAP and AP in SDS micelles, when compared with that in CTAB and
TX micelles. This observation further highlights the efficiencies of these systems
as reporter molecules.
5.3. 11-(4-N,N-Dimethylamino)phthalimido)undecanoic Acid as an Amphiphilic Fluorophore

As the residence of DAP is found to be near the surface, we thought of examining its fatty acid derivative, DAPL where the fluorophore, DAP is attached to its nonpolar end of the fatty acid chain, with the idea that such covalent linkage might help pushing the fluorescing moiety towards the micellar core. Even though such an attempt was unsuccessful in the case of APL, we thought that enhanced hydrophobicity introduced in the fluorophore by methylating the amino group, might be of some help in achieving the objective. The fluorescence spectrum of DAPL in \textit{aq} solution was reported to be unusually broad to suggest the presence of multiple components in the spectrum.\textsuperscript{15} We thought that this could be due to various microenvironments experienced by DAPL. Self-coiling and/or aggregation were considered to be responsible for this behaviour. However, a detailed investigation led us to conclude that aggregation was responsible for this. In our investigations, we have carried out experiments with \( \sim 1 \times 10^{-6} \) M concentrations of the probe molecule such that aggregation did not affect the spectral results.

5.3.1. Spectral Characteristics of DAPL in Homogeneous Media

The spectral data of DAPL in homogeneous media are presented in Table 5.2 and some representative absorption and fluorescence spectra are
Fig. 5.4. Absorption (a) and fluorescence (b) spectra of DAPL in various solvents: \((-\text{O-O-})\) 1,4-dioxane; \((-\text{■■■-})\) tetrahydrofuran; \((-\text{□□□-})\) acetone; \((-\text{■-■-})\) acetonitrile; \((-\text{■-■-})\) methanol. \(\lambda_{exc} = 410\) nm.
shown in Fig. 5.4. The spectral features are found to be quite similar to those of DAP showing more pronounced solvatochromic shifts of the fluorescence maxima than those for absorption, indicating an emitting state that is more polar than the ground state. In hydroxylated solvents, the Stokes shift of the fluorescence maximum is considerably larger than that expected based on the polarity of the medium alone. This behaviour is due to the hydrogen bonding interaction between the probe and the solvents. A plot of the Stokes shift ($\Delta \nu, \text{cm}^{-1}$) vs solvent polarity function ($\Delta \bar{f}$) according to Lippert-Mataga eqn. (sec. 2.1.5) is shown in Fig. 5.5 to depict the polarity and hydrogen bonding interaction effects of the solvents on the emission energy of DAPL. As can be seen from the Figure the hydrogen bonding interaction of DAPL is evident from the enhanced Stokes shift in protic solvents that can not be correlated to the polarity alone. In any given solvent, both the absorption and fluorescence maxima of DAPL are Stokes-shifted with respect to those for APL (Table 3.4). This is presumably due to higher ground and excited state dipole moments of the DAP moiety.
Fig. 5.5. Dependence of the Stokes shift ($\Delta \bar{v}$) of DAPL on the solvent polarity function $A_f$ (sec. 2.1.5) according to the Lippert-Mataga equation (eqn. 2.3). The solvents are 1. 1,4-dioxane; 2. tetrahydrofuran; 3. acetone; 4. acetonitrile; 5. ethanol; 6. methanol; 7. water. The straight line represents the best fit to the data collected only in the aprotic solvents.

The fluorescence yield ($\phi_f$) and lifetime ($\tau_f$) of DAPL as a function of the polarity of the solvent are shown in Table 5.2 along with the calculated rate constants for the nonradiative decay process ($k_{nr}$). It is observed that while $\phi_f$, 

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Tf and $k_{nr}$ values of APL (Table 3.4) remain more or less constant in aprotic solvents, for DAPL, there is a reduction in $\phi_f$ and $\tau_f$ and enhancement of the nonradiative rates on increase of the polarity of the media. This behaviour is consistent with the difference in the behaviour of AP and DAP which has been interpreted due to the existence of a nonemissive TICT state (that acts as a nonradiative decay channel) below the emitting locally excited state of DAP. This additional polarity dependent property makes DAPL a probe superior to APL. In hydrogen bonding solvents, a drastic decrease in $\phi_f$ and $\tau_f$ is observed for both the compounds.
Table 5.2 Photophysical Properties of DAPL in Homogeneous Media.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ET(30)(^\text{a}) (nm)</th>
<th>(\lambda_{\text{max}}^{\text{abs}}) (nm)</th>
<th>(\lambda_{\text{max}}^{\text{flu}}) (nm)</th>
<th>(\phi_f)</th>
<th>(\tau_f) (ns)</th>
<th>(k_{nr}) ((10^7 \text{ s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-dioxane</td>
<td>35.9</td>
<td>384</td>
<td>465</td>
<td>0.66</td>
<td>18.30</td>
<td>0.79</td>
</tr>
<tr>
<td>THF(^\text{c})</td>
<td>37.2</td>
<td>383</td>
<td>469</td>
<td>0.59</td>
<td>15.80</td>
<td>2.58</td>
</tr>
<tr>
<td>Acetone</td>
<td>42.5</td>
<td>386</td>
<td>488</td>
<td>0.340</td>
<td>11.70</td>
<td>5.62</td>
</tr>
<tr>
<td>AN(^\text{d})</td>
<td>46.5</td>
<td>392</td>
<td>504</td>
<td>0.213</td>
<td>7.40</td>
<td>10.60</td>
</tr>
<tr>
<td>BuOH</td>
<td>49.9</td>
<td>395</td>
<td>527</td>
<td>0.037</td>
<td>2.50</td>
<td>38.90</td>
</tr>
<tr>
<td>PrOH</td>
<td>50.6</td>
<td>396</td>
<td>530</td>
<td>0.025</td>
<td>2.10</td>
<td>47.10</td>
</tr>
<tr>
<td>EtOH</td>
<td>51.9</td>
<td>393</td>
<td>532</td>
<td>0.013</td>
<td>1.12</td>
<td>88.20</td>
</tr>
<tr>
<td>MeOH</td>
<td>55.1</td>
<td>395</td>
<td>535</td>
<td>0.006</td>
<td>0.89</td>
<td>111.00</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>63.1</td>
<td>417</td>
<td>575</td>
<td>0.001</td>
<td>0.16 (73.6%)</td>
<td>640.00</td>
</tr>
</tbody>
</table>

\(\text{ET}(30)\) measured using betaine dye. \(\text{Excited at } 410 \text{ nm.}\) \(\text{Tetrahydrofuran.}\) \(\text{Acetonitrile.}\) \(\text{Calculated using relative amplitude.}\) \(R_i = 100B_i\tau_i/\sum_{k=1}^{2}(B_k\tau_k)\).
5.3.2. DAPL as Sensor for Microenvironments of Micelles

5.3.2.1. Spectral Features

Studies have been carried with SDS, CTAB and TX surfactants. No noticeable change could be observed in the absorption spectrum of DAPL on addition of the surfactants to an aq solution of DAPL. A representative absorption spectrum in micellar medium is shown in Fig. 5.6.

Fig. 5.6 displays the fluorescence spectra of DAPL as a function of TX concentration. A blue-shift of fluorescence maxima with an enhancement of the fluorescence yield can be noticed from Fig. 5.6, as has been observed with other AP derivatives. The binding of the fluorophore to a less polar site in the micelle is indicated by these data. The spectral shift and enhancement are observable only beyond a certain concentration of the surfactant and also, at sufficiently higher concentration of the surfactant, there is no change either in the location of the spectral maximum or in the fluorescence intensity indicating that most of the molecules are in bound condition.
Fig. 5.6. 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 labelled 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. \( \lambda_{exc} = 410 \text{ nm} \).
A representative plot of $\phi_F/\phi_0$ of DAPL against the surfactant concentration from which the CMC values of the surfactants have been evaluated is shown in Fig. 5.7. The estimated CMC values are tabulated in Table 5.3. Again, a good agreement with the literature values can be noticed. A summary of the maximum spectral shift and fluorescence enhancement data is also given in the Table 5.3. The $\tau_F$ values of DAPL under completely micellised condition are shown in Table 5.3.
Fig. 5.7. A plot of relative fluorescence intensity of DAPL ($\phi_f/\phi_0$) as a function of CTAB concentration in aqueous solution. The insert shows the variation of the ratio over a larger concentration range.
Table 5.3 Fluorescence Data of DAPL in Micellar Media.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Concentration (mM)</th>
<th>Maximum</th>
<th>CMC (mM)</th>
<th>Kc (M⁻¹)</th>
<th>τ₁ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>φf/φ₀</td>
<td>Shift (nm)</td>
<td>Literaturea</td>
<td>Measured</td>
<td></td>
</tr>
<tr>
<td>SDS</td>
<td>75</td>
<td>7.2</td>
<td>31.0</td>
<td>8.00</td>
<td>7.4</td>
</tr>
<tr>
<td>CTAB</td>
<td>80</td>
<td>9.2</td>
<td>44.5</td>
<td>0.92</td>
<td>0.6</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>128</td>
<td>22.4</td>
<td>54.0</td>
<td>0.26</td>
<td>0.27</td>
</tr>
</tbody>
</table>

a From ref. [1]. b Calculated using relative amplitude, \( R_i = 100 B_i \bar{\eta}_i / \sum_{k=i}^2 (B_{k} \eta_{k}) \). c ± 10%.
5.3.2.2. Binding Ability

The binding constants, evaluated from the fluorescence intensity data using eqn. 3.3, are given in Table 5.3. A typical plot for this probe based on this equation is shown in Fig. 5.8. Considerably higher $K$ values of DAPL when compared to the native probe, DAP with the respective micelles, suggest that the attachment of the fatty-acid chain help better binding of the probe molecule. A similar observation was also noted for APL. 2-4 folds increase in the binding ability of DAPL over that of APL with the micelles show that former is a better probe than the latter.
Fig. 5.8. Plot of \(\frac{(I_\infty - I_0)}{(I_t - I_0)}\) against \([M]^{-1}\) in Triton X-100 for DAPL.

The plot is based on eqn. 3.3.

5.3.2.3. Quenching Studies

Quenching studies have been performed in both \(aq\) and micellar media using aqueous quenchers \(I^-\) and \(Cu^{+2}\) as they are helpful in determining the location of the probe. The plots of the relative fluorescence intensity against the quencher concentrations were found to be linear, indicating the absence of any
significant static quenching over the quencher concentration range used. The quenching data are tabulated in Table 5.4.

Table 5.4 Quenching Data of DAP and DAPL in Aqueous and Micellar Media.

<table>
<thead>
<tr>
<th>Probe</th>
<th>Quencher</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;O</th>
<th>SDS</th>
<th>CTAB</th>
<th>Triton X-100</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAP</td>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>16.2</td>
<td>66</td>
<td>-</td>
<td>2.33</td>
</tr>
<tr>
<td></td>
<td>I-</td>
<td>11.9</td>
<td>118</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DAPL</td>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>18.3</td>
<td>64</td>
<td>-</td>
<td>2.62</td>
</tr>
<tr>
<td></td>
<td>I-</td>
<td>8.1</td>
<td>81</td>
<td>6</td>
<td>-</td>
</tr>
</tbody>
</table>

The uncertainties in $k_q$ values are fairly high as $\tau_0$ values were low and could not be measured accurately with the experimental set-up in this study.

5.3.2.4. Location of DAPL in Micelles

The observed maximum shift and enhancement in micellar media lie between 31-54 nm and 7.2-22.4, respectively. The values are very similar to those obtained for DAP. Therefore, it appears that the DAP moiety of DAPL resides at a site very similar to that resided by the native probe, DAP. The micropolarities estimated for the Solubilisation site of the probe are 56.9, 54.4 and 52.7 (in $E_T(30)$ scale) for SDS, CTAB, and TX, respectively. These values are again very close to the micropolarities sensed by DAP in respective micellar microenvironments.
It can be seen from the quenching data presented in Table 5.4 that both I⁻ and Cu⁺² are good quenchers of DAP and DAPL fluorescence in \textit{aq} medium. Secondly, the quenching rates of DAP and DAPL with Cu⁺² and I⁻ in anionic (SDS) and cationic (CTAB) micelles, respectively, are considerably higher due to high local concentration of the quencher ions near the surface because of electrostatic attraction. In neutral micelles, TX where electrostatic forces are absent, the quenching rate constant is quite lower than that in \textit{aq} medium, suggesting lesser accessibility of probe molecules towards the quenchers. Finally, the similarity of the quenching data of DAPL and DAP clearly suggests that the location of fluorescing moiety in the former is very similar to the later in micelles. Therefore, it is concluded that the binding of DAPL with the micelles is very similar to that of APL (as depicted in Fig. 3.12) i.e. folding of the hydrocarbon chain brings the terminal fluorescing moiety near the surface.

DAPL is proved to be a potential indicator to follow the micellisation process irrespective of the charge of the micelle. In terms of sensitivity, as was expected, dimethylamino derivatives are superior to their amino counterparts. Chain folding appears to be a general phenomenon for AP or DAP fluorophore labelled fatty acids.

5.4. References


