CONCLUDING REMARKS

The conclusions drawn from the investigations reported in the thesis are presented in this chapter. The scope of further work that could be carried out based on the present findings is also briefly discussed.

The work embodied in the thesis describes the Photophysical behaviour of some fluorescent electron donor - acceptor (EDA) systems in homogeneous and micellar media. The highly sensitive fluorescence properties of 4-aminophthalimide (AP) and 4-N,N-dimethylaminophthalimide (DAP) on the polarity of the surrounding environment have been made use of in studying the microenvironments of the simplest membrane mimetic systems, micellar media. It has been shown that the aggregation of the surfactant molecules in aqueous solution can be very conveniently followed by monitoring any one of the following emission parameters of AP, fluorescence intensity, lifetime or position of the band maximum. It is of interest to note in this context that the ability of the AP derivatives to follow the micellar aggregation is not limited by the micellar charge. In this respect, the AP derivatives are found to be superior to many ionic EDA fluorescent systems. One of the several parameters that characterises a micellar aggregate, critical micelle concentration (CMC), has
been evaluated for three types of micelles using AP. The measured values are found to be in excellent agreement with the literature values. It has been unambiguously established that AP can always be located at the micelle-water interfacial region. This preferential location of the fluorescence probe-molecule at the interface is found to be the result of a combination of hydrogen bonding interaction of AP with the water molecules and its hydrophobic interaction with the micelles. The interfacial polarities of the anionic, cationic and neutral micelles, quantitatively measured using AP as fluorescent probe, in terms of microscopic polarity parameter, $E_T(30)$, show a rather small variation with the charge of the micelles.

A new amphiphilic fluorophore, APL has been developed, in which the AP fluorophore is covalently labelled to the nonpolar terminal group of a fatty acid, in an attempt to design fluorescence probe for the deeper core region of the micelles. The Photophysical properties of this system in homogeneous media are found to be quite similar to those of AP. In micellar media, however, APL shows stronger binding with the micelles. Even though the binding of APL with the micelles is found to be stronger than with AP, interestingly, the changes of the fluorescence properties of APL on micellisation are not found to be drastically different from those observed with AP. Fluorescence quenching studies suggest that despite its covalent attachment with the nonpola tail of the surfactant molecule, the fluorescing moiety of APL can still be located at the interface. Chain folding of the polymethylene spacer of APL has been proposed
The photophysics of two Carbostyril laser dyes, Cl 24 and Cl 65, which are structurally and electronically similar to extensively studied coumarin dyes, has been studied as a function of the solvent polarity to find out whether keto-in micellar media to account for this observation. Strong hydrogen-bonding affinity of the carbonyl groups of the fluorophore seems to be the driving force for this type of behaviour.

The studies involving DAP and DAPL reveal clearly the superiority of the DAP fluorophore compared to the AP fluorophore in sensing the hydrophobic regions of the micellar structure. The existence of a low-lying nonfluorescent TICT state below the fluorescent ICT state and enhanced hydrophobicity of the DAP fluorophore seem to account for the observed photophysical behaviour of the compounds. Chain folding, as observed in the case of APL, has also been demonstrated in the case of DAPL.

A series of new n-(4-aminophthalimido)alkane derivatives have been synthesised and fully characterised with a view to understand their photophysical behaviour in homogeneous media. Studies on these systems have led to some interesting observations particularly in aqueous media. For systems with large alkyl groups, the polarity sensed by the fluorophore in aqueous media is found to be considerably different from that of water. It has been shown that even at very low concentration, these molecules readily aggregate in aqueous solutions. The emission observed from these aggregates is found to be considerably different from that of the bare fluorophore in the same medium.

The photophysics of two Carbostyril laser dyes, Cl 24 and Cl 65, which are structurally and electronically similar to extensively studied coumarin dyes, has been studied as a function of the solvent polarity to find out whether keto-
enol tautomerism and internal rotation (twisting) of the amino or dialkylamino group plays any role in influencing the Photophysical behaviour of these systems. The experimental studies have been supplemented by semi-empirical theoretical calculations. The results of this investigation reveal that the keto form of the Carbostyrils is the only dominant form, both in the ground and excited state. Further, unlike in coumarins, twisting of the dialkylamino group is found have no influence on the photophysics of the Carbostyrils. A reinvestigation of the fluorescence properties of a few coumarin dyes seems to be necessary based on the present findings. The preliminary investigation carried out to investigate the potential of the Carbostyrils as fluorescence sensors for micellar media reveals that although these systems can be used to follow the microheterogeneous environments, the fact that the magnitudes of the changes of the fluorescence properties are not very appreciable suggest that the Carbostyrils are not very promising systems among the EDA molecules.

The fluorescence behaviour of a dimeric species N,N'-bis(4-carbomethoxyphenyl)piperazine has been investigated in media of different polarities to determine the excited state dipole moment of this kind of highly symmetrical systems. The X-ray diffraction studies confirmed a highly symmetrical structure of the system in the ground state. On the other hand, the fluorescence data clearly indicate that the ground state symmetry of the molecule is lost in the excited state. It is argued that twisting alone can not account for extremely high dipole moment of the molecule in the excited state. Structural
changes in the piperazine ring seem to be necessary to account for the experimental findings.

Since hydrogen bonding interaction with water molecules is primarily responsible for the location of the fluorescent AP moiety at the micelle-water interface the development of AP-based fluorescence probe molecules for the nonpolar micellar core region requires development of systems where the hydrogen bonding interaction of the fluorophore with the solvent is prevented. Since the carbonyl groups of AP are found to be involved in hydrogen bonding interaction with water molecules, one can probably achieve this objective by designing systems in which the carbonyl groups are engaged in intramolecular hydrogen bonding interaction with appropriate groups (such as -OH group) at 3 and 6 positions of AP. This is one direction where further studies are to be made.

As hydrogen bonding interaction is also responsible for chain-folding in surfactant-linked systems, APL and DAPL; the structural modification as stated above might also help preventing such folding of the polymethylene groups. This aspect needs to be studied.

The investigations have been carried out only in membrane mimetic simple model systems. The present results will be useful in understanding more complex media of biological relevance such as membranes and proteins. Such studies are required to be undertaken.
The TICT model has recently been criticised and a new model has been proposed according to which a change in the hybridisation of the amino nitrogen is responsible for the nonradiative decay of the fluorescent LE state and long-wavelength fluorescence band of DMABN. It is therefore necessary to re-investigate the Photophysical behaviour of dimethylamino derivative of AP to find out whether it can be understood in terms of the newly-proposed mechanism.

The results obtained with the dimeric molecule raises interesting possibilities. Further studies are necessary to find out the exact nature of the structural changes associated with the electronic excitation of the system.