CHAPTER 1

INTRODUCTION

This chapter gives a brief introduction on the photoinduced charge separation process with emphasis on twisted intramolecular charge transfer (TICT) phenomenon. Subsequently, fluorescence studies on the micellar media are summarised briefly. The chapter ends with a description of the motivation of the present work and the layout of the thesis.

1.1. Photoinduced Charge Separation at Molecular Level

Photoinduced charge separation (PECS) reactions occupy a central position in the chemistry of life. Over the past decades, a significant effort has been devoted to the study of PECS as a means of capturing and storing solar energy.\(^1\) Photoinduced energy and electron transfer processes in artificial multicomponent systems are currently the object of extensive studies.\(^2\) The interest on these processes can be related to the following goals: i) a better understanding of natural photosynthesis;\(^3\) ii) the design of supramolecular luminescent systems capable of sensing environments;\(^4\) iii) the construction of nanometer scale wires,\(^5a\) switches,\(^5b\) logic gates,\(^5c\) and other components for
the development of molecular electronic devices. The development of non-linear optical materials is also primarily based on charge-transfer phenomenon.

Mulliken introduced the concept of the charge transfer transition to describe the spectral and bonding interactions of molecular complexes formed between an electron donor and acceptor. Weller was first to show that a charge-transfer complex can be formed between an excited and a ground state species, even though no complex formation could be detected in the ground state. Such an excited molecular complex is termed as exciplex. In systems involving flexible spacers, the charge transfer complex or exciplex is often formed by conformational changes occurring in the spacer, where the donor (D) and the acceptor (A) moieties come closer, thus allowing charge transfer to occur by D-A orbital overlap. In systems with limited conformational flexibility, where through-space interaction of the D and A orbitals is not possible, the charge separation can take place as a result of through-bond interaction of the D and A orbitals. There has been considerable effort thorough model systems comprising electron D and A groups linked covalently through \( \pi \) or \( \sigma \) bond to investigate the dependence of the electron transfer rates on the free energy of reaction, D-A distance, orientation and solvent. PECS has also been studied in great detail in an attempt to minimise the back electron transfer steps so that these materials could be useful for molecular devices. Many systems are reported in the literature to demonstrate that efficient PECS can occur over large distances. One of the most spectacular of which is to be
found in the photosynthetic reactions centres of certain photosynthetic bacteria.\textsuperscript{14}

Since charge separation on a molecular level is often involved, the study of the model systems displaying charge separation is essential to understand the mechanisms involved. In the fortuitous case of luminescent charge transfer (CT) state, the CT emission provides an excellent opportunity to monitor their dynamics because internal and environmental influences affect this luminescence in characteristic way yielding detailed information on their thermodynamic, kinetic and other Photophysical and even photochemical properties of such species. The Photophysical techniques such as steady-state, time-resolved fluorescence and transient absorption studies are useful to detect the CT states. Luminescent molecules are also known for their extensive utility in the study of molecular organisation and dynamics in macromolecules \textsuperscript{15,23} and organised assemblies such as proteins,\textsuperscript{16,19,23} micelles, \textsuperscript{17,22,23} cyclodextrins and membranes etc.\textsuperscript{16-23}

1.2. Twisted Intramolecular Charge Transfer Phenomenon

Over past three decades there has been considerable interest in the Photophysical properties of the D-A compounds formally linked by a single bond.\textsuperscript{23-26,28} Since the first report by Lippert\textsuperscript{26} on dual fluorescence exhibited by p-(dimethylamino)benzonitrile (DMABN), a vast number of studies have been devoted to elucidation of the mechanism of the intramolecular charge
transfer (ICT) emission in systems where the D and A moieties are linked by a single bond. Lippert originally proposed that there are two excited states, a highly polar state (A band, $^1L_a$ state in Platt's notation) and relatively nonpolar state (B band, $^1L_b$, state), responsible for the long and short wavelength emission, respectively. Later Grabowski et al. on the basis of experimental studies on model compounds such as 1-4, proposed the TICT concept to account for the dual-luminescence. According to this hypothesis, the primary excited state of D-A molecules (for e.g., p-dialkylamino derivatives of benzonitrile) converts to a highly polar fluorescent state with a mutually perpendicular confirmation of the $D^+$ and $A^-$ moieties. The $\pi$-electronic decoupling of the $D^+$ and $A^-$ moieties leads to a full charge separation and consequently, to a large dipole moment and a considerable solvent reorientational energy. Dual luminescence is believed to be due to the emission from the substrate.
locally excited (LE) state (planar conformation) and the product TICT state (twisted conformation). The energetic situation, as can be extracted from the spectra of DMABN and related compounds, is depicted in Fig 1.1.

Fig. 1.1. A schematic representation of the TICT phenomenon.
There have been numerous studies, on a wide variety of systems, primarily for the verification of the TICT mechanism. Observation of TICT like emission from the molecules already twisted in the ground state, absence of the second emission in rigidized systems,\textsuperscript{29} consistency of the excited state dipole moment with a large degree of intramolecular separation of charge,\textsuperscript{30} observation of radical anion in transient absorption spectroscopic measurements,\textsuperscript{31} observation of dual fluorescence in vapour phase\textsuperscript{32} and many others\textsuperscript{23,24} have given this mechanism a strong basis. Apart from molecules containing dialkylamino or arylamino groups, TICT is reported for a host of other molecules, e.g. biaryls, amides etc.\textsuperscript{1,2} and recently for 3H-indoles.\textsuperscript{33} Even though dual emission is observed for many compounds, a non-emissive TICT has also been proposed in many cases.\textsuperscript{34,35,127}

Several other models have been offered in the literature to account for the dual emission in DMABN and its derivatives, e.g. solute-solvent exciplex formation,\textsuperscript{36} the so called pseudo-Jahn-Teller coupling effect and/or change in pyramidalisation of the amino nitrogen\textsuperscript{37} and the recently proposed model that assumes a bending of the cyano group.\textsuperscript{38} Some of these models have been criticised.\textsuperscript{39,40}

The most important feature of the TICT states is the transfer of exactly one unit of electronic charge from D to A which can be verified by experimental measurement of the dipole moment of charge separated species. A number of external and internal factors influence the TICT formation rate. The electron
donor and the acceptor strength of the substituents, ground state twist angle, rotating volume of the twisting group and molecular shape are some of the factors which determine the rate of TICT formation. An increase in the polarity is expected to stabilise the TICT state by solvation and hence should favour the TICT process. To account for the observation of an increase in the TICT rate increase with increase in the polarity of the medium, Eisenthal et al. proposed a polarity dependent activation barrier ($E_g$) which decreases linearly with increase in polarity as in eqn. 1.1, where $E_T(30)$ is the microscopic polarity parameter (defined in sec. 2.1.1) and $E_B^0$ is the barrier in a hydrocarbon having an $E_T(30)$ value of 30 kcal/mol.

$$E_B = E_B^0 - A[E_T(30) - 30]$$

1.1

Thus the overall rate, $k_T$ is given by eqn. 1.2.

$$k_T = k_T^0 \exp \left(-\frac{E_B^0}{RT}\right) \exp \left[A\{E_T(30) - 30\}/RT\right]$$

1.2

This relation accounts for a linear relation between $\log k_T$ and $E_T(30)$. Increase in viscosity is likely to hinder the twisting motion, thereby retarding the TICT process. Pressure also affects the rate of TICT process as it changes the solvent viscosity and dielectric constant which play a vital role in determining the rate.
The dramatic dependence of the TICT process on solvent polarity has attracted a large number of theoretical studies on the solvents effects on TICT, classified as stochastic models and quantum chemical methods. In the stochastic models, the overall rate is obtained by statistical treatment or mechanical model (e.g. Langevin equations) incorporating the solvent effect as a friction term. The second approach is based on quantum chemical calculation of the potential energy surface with twist angle as the reaction co-ordinate for isolated molecules and in the presence of solvents. The semi-empirical calculation based on various methods such as INDO, MNDO, CNDO and AMI methods and ab initio studies have been performed to describe the anomalous behaviour of DMABN and similar systems. Most of the calculations support the TICT mechanism.

1.3. An Introduction to Micelles

The organised systems can be broadly classified into three types: 1) organised assemblies composed of surfactants and lipids such as micelles, vesicles, liposomes, mono and multilayers, microemulsions, and liquid crystals; 2) supramolecular host systems with large cavities capable of accommodating small guest molecules and ions such as zeolites, clays and cyclodextrins etc.; 3) adsorbed molecules on reactive and non-reactive surfaces e.g. silica, porous glass etc. These systems are generally called 'microheterogeneous' to indicate their heterogeneous character at the microscopic level with the presence of
interfaces separating distinct hydrophobic and hydrophilic domains. A good majority of these systems provide optically clear solutions readily amenable to photochemical studies. Organised surfactant aggregates, micelles, microemulsions etc. have been extensively exploited for developing chemistry based on membrane-mediated processes. Micelles have been proposed as simple model systems for a variety of important two-phase systems such as monolayers, colloids, proteins, enzymes and membranes. Micelle-water interface incorporates the dielectric asymmetry and microenvironments typical of other interfacial systems, thus extremely useful for posing and answering problems regarding microenvironments encountered in interfacial systems of other complex systems of biological interest. The formation of micelles is one of the most spectacular example of hydrophobic interactions. Therefore, simple micelles provide models for the investigation of hydrophobic interactions, a crucial problem in understanding the stability of biologically important molecules such as protein. Organisation and compartmentalisation in membrane mimetic systems have been exploited for reactivity control, molecular transport, recognition, artificial photosynthesis and target-directed drug deliveries. Lastly, but not leastly, organised surfactant assemblies, as the term membrane mimetic implies, can be considered to mode structures and interactions in real membranes.

Micelles refer to aggregates of surfactant molecules of colloidal dimensions and implies a situation in which these aggregates are in mobile
equilibrium with the molecules or ions from which they are formed, i.e. a micelle is a dynamic structure which exists in equilibrium with its monomer. Depending on the chemical composition, micelles can be non-ionic, ionic or ampholytic. Aggregation behaviour depends on the nature and length of the hydrocarbon chain, the head group, concentration, temperature and other additives.\textsuperscript{54, 55} A schematic sketch of different possible structures of micelles is shown in Fig. 1.2.

Fig. 1.2. Different structures of micelles and mesophase.
The concentration at which micelles appear corresponds to the critical micelle concentration (CMC). However, the change occurs, over a narrow concentration range rather than a precise point and the magnitude of the range depends somewhat on the physical property being measured. For detergents containing long-chain hydrocarbon groups, the CMC value is usually between $10^{-4}$ and $10^{-2}$ M. The addition of strong electrolytes reduces the CMC of ionic surfactants but only slightly alters that of nonionic surfactants. Effects of temperature and other factors which alter the CMC are helpful in investigation of micellar catalysis, inhibition, or hydrophobic interactions. The number of monomers in the aggregate, the aggregation number (N) determines the size and the geometry of the micelle and hence an important quantity. N ranges for surfactants of 10-18 carbon atoms in aq medium generally between 10-150. Like CMC, N is also dependent on the concentration of the surfactant, additives and on the temperature. The conventional methods for the determination of N are light scattering, diffusion, viscosity, NMR and fluorescence techniques.

The common picture of a micelle is quite similar to Hartley's original notion of an oil droplet in a polar coat. At CMC, the aggregation begins which grow rapidly over a very limited concentration range to a size which for a given surfactant remains approximately constant with further increase in surfactant concentration. Fig. 1.3. shows the conventional representation of the micelle formed by ionic detergents. Typically such micelles have an average radii of 12-13 A containing 20-100 monomers. Depending on the head group
structure, concentration and other experimental variables, the micelle may be roughly spherical, ellipsoidal, disk-like or **rod-shaped**. Spherical at low concentration and rod-shaped at high concentrations is found to be the case for a wide variety of ionic surfactants. The hydrophobic part of the aggregate forms the 'core' of the micelle which is liquid-paraffin like in character while the polar...
head groups are located at the micelle-water interface in contact with and hydrated by a number of water molecules. The charged head groups and the small counterions of the ionic micelle are located in a compact region known as the 'Stern layer', which extends from the core to a few angstroms beyond the shear surface of the micelle. The compactness of the Stern layer is responsible for the reduction of the net charge on the micelle and is an extremely anisotropic region with properties intermediate between those of water and hydrocarbon (alcohol-like is the common description of its polarity). The remaining counterions are however, located outside the shear surface forming diffuse 'Gouy-Chapman' electrical double layer where they are completely dissociated from the charged aggregate and are able to exchange with the ions in the bulk of the solution. The structure of the small globular micelles formed at low surfactant concentrations is a matter of ongoing and lively debate especially with regard to the question of water penetration in the micelle. Hartley's model cannot be reconciled with any appreciable water-to-hydrocarbon contact. Experimental studies do indicate that depending on the micelle type, water appears to penetrate the micelle to various depths. There have been other models from Dill and Flory, and recently Menger's reef model which proposes a loose, porous, and highly disordered cluster comprising of hydrocarbon chains and water. Molecular dynamics simulation method is also being used to investigate the microstructure of micelles theoretically.
Formation of association colloids is not restricted to aqueous solutions. In non-aqueous media, certain amphiphilic molecules, such as sodium bis(2-ethylhexyl)sulfosuccinate (AOT), assemble to form reverse micelles aggregation in which the polar heads of the amphiphile cluster to form a micellar core and the hydrophobic tails extend into the organic bulk phase. The structure of a reverse micelle in a nonpolar media is shown in Fig. 1.4. The distinguishing feature of these inverted micelles is their ability to solubilize large amounts of water in the inner core. The ability to control the size of the water pool and the properties of the water present therein itself is a unique feature that a good

Fig. 1.4. Structure of reversed micelle.
majority of studies in reversed micelles are devoted to the characterisation of waterpools (size, polarity, viscosity, etc.) and exploitation of various chemical reactions in these waterpools. The waterpool is an interesting model candidate to mimic the water pockets that are often found in various bioaggregates such as proteins, membranes, etc.  

1.3.1. Fluorescent Systems for Study of Micellar Media

A considerable amount of effort has been directed over the past decades in determining the physio-chemical properties of self-assembled surfactant aggregates using physical methods such as X-ray, small angle neutron spectroscopy, nuclear magnetic resonance spectroscopy, light scattering etc. Photophysical methods stand apart for their wide scope and extreme sensitivity at very low solute concentrations which is necessary for least perturbation of the host system by the guest molecules. 15-23,56,71,72 Luminescence probes can be thought of as sensors of microenvironments. The photons emitted by such probes are reporters of the local structure in the vicinity of the probe at the time of emission. The basic notion behind the use of a luminescent probe is that luminescence parameters, sensitive to changes in the microenvironments will display experimentally distinct luminescence properties which will characterize uniquely each environment. The various luminescence parameters that are used in this context are the location ($\lambda_{\text{max}}$), intensity ($\phi$), lifetime ($\tau$) and polarisation ($P$) of the emission. The measured changes in a luminescence probe have been
related to the properties of the environment of the probe as i) polarity; ii) viscosity; iii) diffusion; iv) partitioning between phases; v) roughness of the micelle surface; vi) degree of water penetration into these aggregates; vii) concentration of quenchers and viii) distance between groups.

A variety of probes are documented in the literature whose fluorescence characteristics are altered by the environment for a variety of reasons (polarity, viscosity, pH etc.). The structures of a few commonly used fluorescence probes are shown in Fig. 1.5. The properties or the parameters of the micelles that are most commonly measured by employing fluorescence probes are CMC, mean solvent properties such as polarity and viscosity measured in terms of effective dielectric constant (ef) or $E_T(30)$ and apparent micro viscosity, $\eta$, respectively, degree of water penetration and mean electrostatic surface potential ($\psi$). The various commonly used fluorescence probes can be classified as follows.

1.3.1.1. Probes Based on Ham Effect

Condensed aromatics such as Py (1) show fairly well-resolved fluorescence spectra in solution. Variation of solvent leads to a large variation in the intensities of the vibronic bands without much spectral shift and the phenomenon is known as Ham Effect. For Py, the peak intensity ratio of the vibronic bands I and III serves as a sensitive guide of the environmental
Fig. 1.5. Chemical structures of some commonly used fluorescence probes.

contd....
micropolarity and this has been used to evaluate the different parameters relating to micellar aggregates. Important among them are CMC values of the micelles, polarity of the interfacial region, water penetration into the micelles. Zachariasse et al employed amphiphilic molecules such as Py-(CH₂)n-COOH and Py-(CH₂)n-N(CH₃)₃Br⁻ to show that the pyrenyl group penetrates more and more into the interior of the micelles when n increases from 3 to 15. The polarity of the direct probe environment decreases from a value somewhat larger than that of methanol for Py-(CH₂)₃-COOH solubilised in surface region of the micelle, to a value approaching that of hexadecane for the

Fig. 1.5. Chemical structures of some commonly used fluorescence probes.
central region of the micelle (e.g. SDS) for n-15. It is concluded that the water content in the micelles decreases when going from the surface region to the micellar interior and the later was found to be free of water molecules.

The bile salts are among the most important biological detergent-like molecules and aggregation in \textit{aq} solution has been investigated using Py monomer fluorescence\(^\dagger\) The utility of the I/III peak ratio of Py emission as a probe for determining the pressure effect on CMC was demonstrated by Hara et al\(^7\) at high pressures. Frindi et al\(^7\) have found that the CMCs of amphoteric surfactants n-octyl, n-decyl DPSs are much higher than expected for surfactants with zero net charge using Py probe. The presence of polymers induces the aggregation behaviour of surfactant well below the CMC, referred to as critical aggregation concentration (CAC). Recently, this has been studied using Py probe in presence of nonionic polymer, PVA and highly co-operative nature of the aggregation has been concluded from peak ratio variation.\(^8\) The interfacial polarities, \(\varepsilon_f\) of the mixed systems CT AB/PPG estimated to be 17 and 13 for M.W=425 and 1000, respectively.\(^8\) Py fluorophore has also been used to study 1:1 CTAB/\(\beta\)-CD complex aggregates.\(^8\)

1.3.1.2. Probes Based on High Excited State Dipole Moment

In certain cases, the dipole moment of the excited state is significantly higher than that of the ground state. As a consequence, the emission maxima (\(\lambda_{\text{max}}\)) and yield (\(\phi_f\)) depend on the \textit{polarity} of the solvent. Usually an empirical procedure of comparison of the emission spectra of the probe in
different solvents with those obtained in the organised media is used for the evaluation of microenvironmental polarity. Examples of this kind of probes are ANS (2), TNS (3), DNSC (5) and NPN (6). These probes show a large variation in $\lambda_{\text{emi}}^{\text{max}}$ and $\phi_f$ with solvent polarity which serves as an indicator of the surrounding the microenvironment. Recently, Narang et al. have introduced a new hemicyanine polarity probe whose emission behaviour is extremely sensitive to polarity. The increase in $\phi_f$ and blue shift of $\lambda_{\text{emi}}^{\text{max}}$ of ANS with formation of micellar aggregates was monitored to estimate the CMC values of nonionic and SDS surfactants. The interfacial polarity of nonionic and zwitterionic micelles was found to correspond to the polarity of 70% ethanol-30% water mixture from ANS fluorescence. This probe was also used in testing the environment of AOT reversed micelles when the volume of the water core was varied. TNS has been shown to be a potential indicator for following the micellisation of different surfactants in the absence and the presence of salt. Kano et al. used dansyldecylamine as probe to conclude that the fluorescing moiety could be located near the surface of the micelles.

Recently, Melo et al. used 12-AS to probe the water content of cationic and anionic micelles. Very recently, Sarkar et al. have studied the solvation dynamics of coumarin 480 in AOT/n-heptane/water, in neutral (TX-100), cationic (CTAB) and anionic (SDS) micelles showing that the dynamic properties of the water molecules in water cluster of reversed micelles and Stern layer of the normal micelles were appreciably different from those in bulk water.
The structure of the AOT reverse micelles in near-critical and supercritical fluids has sparked significant interest which has been investigated using fluorophores such as prodan and ANS.87

1.3.1.3. Probes Based on Solvent Effects on \((n,n^*)\) and \((\pi, \pi^*)\) States

Presence of low-lying closely-spaced \((n, \pi^*)\) and \((\pi, \pi^*)\) levels is a common feature in the photophysics of organic heterocycles. As \((\pi, \pi^*)\) and \((n, \pi^*)\) states respond differently to the polarity of the medium, in molecules that have the \((n, n^*)\) state as the lowest energy in nonpolar solvents, there can be inversion in the nature of the lowest excited state in polar solvents leading to drastic changes in fluorescence efficiency. Fluorophores PyCHO (4),88 and 7-alkoxycoumarin (7) show this type of behaviour. Nile red also has recently been shown to be an excellent fluorescence probe of this class.89

The strong solvent polarity dependence of the fluorescence of PyCHO has been excellently exploited to probe the polarities of a number of various micelles. As this molecule was found to sit at the micelle-water interface, it served for the estimation of interfacial polarities of micelles.88 Turro et al.88b have studied the variation the interfacial polarities of SDS, CTAB and CTAC micelles with pressure. PyCHO was also reported to be an ideal fluorophore for CMC evaluation.88c Solvent dependent \(\phi_f\) values of 7-alkoxycoumarins was found to be useful in measuring the CMCs and also the surface polarities of the micelles formed by ionic (SDS, CTAB) and non-ionic (TX-100) detergents.90 Using picosecond emission spectroscopy, the dynamics of the ICT process of
nile red inside the water pool of AOT/n-heptane microemulsions has been studied recently. 91

1.3.1.4. Donor-Acceptor Molecules with TICT States

A few organic molecules with D and A moieties linked by single bond exhibit dual fluorescence originating from planar ICT (short \( \lambda \) band) and perpendicular TICT states (long \( \lambda \) band). Fluorescence originating from the TICT state is highly sensitive to the solvent polarity due to the large dipole moment arising from the perpendicular conformation of the D\(^+\) and A\(^-\). Examples of probes of this category could be found in a recent review article.23 Systems such as DMABMN (8) display fluorescence that is remarkably sensitive to the polarity and viscosity of the microenvironment. Hence many probes of this class find application in the measurement of micropolarity as well as microviscosity.92,93

High surface roughness and porous nature of SDS micelles have been suggested from a study of the polarity and viscosity dependent fluorescence properties of several 3H-indole derivatives in SDS and CTAB micelles.94a,b These derivatives have also been employed for the study of reverse micelles.94c Very recently, BSA-SDS aggregates have been investigated using ED AC. 95

1.3.1.5. Probes Sensitive to Hydrogen-Bonding Effects

There are certain fluorescent probes such as xanthene dyes (9) (e.g., rose bengal and erythrosin) whose absorption and emission properties are particularly sensitive to the hydrogen-bonding ability of the solvent.96 These probes show a
drastic increase in \( \tau \) in going from a protic to polar a aprotic media. The effect has been used in probing hydrogen bonding capabilities of and water penetration into the microenvironments of organised media. Acridine, methyl 9-anthroate, 4-aminophthalimide are systems belonging to this class.

Molecules undergoing excited state proton transfer (ESPT) often exhibit dual emission, with the normal one arising from an excited species similar in geometry to that in ground state while the Stoke's-shifted emission originates from a tautomer formed in the excited electronic state. The normal and tautomer emission depend crucially on the conformation of the molecule, polarity and hydrogen bonding ability of the solvents. A recent finding indicates that fluorophores which display ESPT can serve as sensitive probes for exploring microenvironment and phase transitions in micelles, and for estimation of CMCs. 3-HF, HPBI (24) and 7-azaindole are examples of this kind.

1.3.1.6. Probes for Environmental Rigidity

Stilbenes and higher polyenes in general represent a group of molecules whose fluorescence properties are very sensitive to the environmental rigidity. Trans-stilbene, for example, is only weakly fluorescent (\( \phi \approx 0.05 \)) and cis-stilbene is non-fluorescent in fluid solutions at room temperature. But in rigid environments both compounds are highly fluorescent (\( \phi \approx 0.75 \)). Whitten and co-workers have used several surfactant derivatives of stilbenes as probes. Fromherz et al. have introduced amphiphilic stilbazonium dye and
hemicyanine dyes of similar kind. AuO (10) is another excellent example of a viscosity sensitive probe. The $\phi_f$ of this system is sensitive to the viscosity of the medium as it affects the internal rotation of the dimethylamino groups, the main cause of the deactivation of the excited state. Rhodamine B is also a viscosity sensitive probe.

As the $\phi_f$ of cis and trans stilbenes, in particular the surfactant stilbenes, depends on the fluidity of the environment, the effect has been studied by Suddaby et al to show that the fluidity decreases in the order of homogeneous hydrocarbons > micelles > vesicles. Similar report has been obtained from aminostilbazonium dye fluorescence. AuO is found to be a good probe for the determination of CMCs and $\eta$ of various micelles.

1.3.1.7. Other Fluorescent Probes

Apart from the types of probes already discussed, one can find a few other fluorescent systems which are used for studies in organised media. Fluorescent pH indicators such as NpOH (11), PyTS (12) and proflavin have been extensively used to investigate the proton donor-acceptor character of the microenvironments and the electrical potential at the surface of the charged interfaces.

Since excimer formation is viscosity dependent, a number of systems which form inter or intramolecular excimer are used to measure the microviscosities of micelles including bile salt micelles. Probes involving Py are most commonly employed for this purpose.
Monitoring the depolarisation of solubilised probe fluorescence often allows the determination of the microviscosity of probe environment. Both steady-state and time-resolved fluorescence depolarisation measurements have been used to measure the microviscosities of organised media. Fluorescence polarisation studies of 2-MeAn, Pe, n-AS, rhodamine B, PyTS, PTC, ANS, TNS and very recently SDU probe in various organised media are examples of this kind.

1.4. Motivation of The Present Work

The main objective of this investigation is i) to exploit the sensitivity of the fluorescence properties of already known EDA molecules to study the microenvironments of the organised media such as micelles and to modify or design them with enhanced ability as sensors for microenvironments and ii) to study the Photophysical behaviour of some new EDA molecules which may have potential as sensors or reporter molecules. The effective use of fluorescence probes requires a detailed knowledge of the nature of the radiative and radiationless transitions and of the mechanism of the interaction of the excited state with different environments. Fluorescent EDA molecules form an important class of candidates for probing microstructural aspects of organised media.

Aminophthalimides are known for their spectral sensitivity towards minor changes in the physical properties of the environment. During the
study of EDA molecules,\textsuperscript{124-127} it was observed that the fluorescence properties of 4-aminophthalimide (AP) were extremely sensitive to the polarity of the media, in particular to the hydrogen bonding solvents.\textsuperscript{124,127} The emission properties of dimethylamino derivative of AP i.e. 4-N,N-dimethylaminophthalimide (DAP) were found to be even more sensitive to the polarity of the medium when compared with those for AP. This is due to the existence of a non-fluorescent TICT state below the ICT emitting state of DAP.\textsuperscript{127} Thus qualifying to act as probes for microstructures, we prompted to use AP and DAP as fluorophores to investigate the structural aspects of organised systems among which the micellar systems are the simplest ones of biological models. Therefore, studies have been carried out using these polarity sensitive probes. The results show that aminophthalimides can act as excellent probes for following the aggregation behaviour of the surfactants. Polarity of the binding sites have been evaluated from the spectral data. AP is found to be a good probe for the interfacial region of the micelles.

Further, to develop probes for the core region of the micelles, new amphiphilic probes, 11-(4-aminophthalimido)undecanoic acid (APL) and 11-(4-N,N-dimethyaminophthalimido)undecanoic acid (DAPL) have been synthesised where the fluorophores AP and DAP are integral part of the respective amphiphiles. Mode of binding and Solubilisation site have been examined for these probes in micellar media apart from their ability to follow micellisation.
While investigating the fluorescence decay behaviour of the surfactant fluorophore, APL, it was observed that the fluorescence decay of the system in aqueous medium as biexponential with long-lived component along with the expected short-lived species. It is known that in aqueous and aqueous-organic binary mixed solvents, hydrophobic interactions force molecules with long hydrocarbon chain to aggregate or self-coil. To find out the origin of the unusual long-lived second component a series of AP-labelled alkanes (APn) with different hydrocarbon chain length have been synthesised and their fluorescence behaviour has been observed in different media.

Among the new EDA systems, we have studied the photophysical behaviour of two structurally related systems, Carbostyril 124 and Carbostyril 165 (C124 and C165) which are used as laser dyes. The focus of this investigation is to find out the possible role of the TICT state, if any, on the fluorescence properties of these systems. This was considered necessary in view of similarity (structural and electronic) of the these systems with the extensively studied coumarin dyes C1 and C120, the latter is known to possess a low-lying non-fluorescent TICT state that affects its fluorescence properties. Theoretical study based on semi-empirical AM1 method has been performed on C124 and C165 to confirm our experimental results. Despite the possibility of the existence of Carbostyrils as keto-enol tautomers, the keto form is shown to be the only absorbing and emitting species. The likely use of these systems as probes for the organised media has been investigated.
A symmetrical dimeric species, N,N'-bis(4-carbomethoxyphenyl)benzoate (BIMBP) has been synthesised and its fluorescence behaviour is studied in media of different polarities to find out whether structural changes in the excited state of this highly symmetrical system could lead to the formation of dipolar species.

1.5. Layout of The Thesis

The 2nd chapter of the thesis gives the experimental details of this investigation. The 3rd chapter presents the results of the investigation carried out on AP and APL in micellar media. Chapter 4 describes the study of the AP-labelled compounds in polar media. Chapter 5 describes the results obtained for DAP and DAPL in micellar media. Chapter 6 is divided into two sections, the first of which concerned with the study of the Carbostyril dyes and the second one describes the fluorescence behaviour of BIMBP in homogeneous media.

Glossary

ANS - 1-Anilinonaphthalene-8-sulfonate
nAS - n-(9-anthroyloxy)stearic acid, n= 2, 6, 9, 12
Au O - Auramine O
nADPS - n-Alkyl(dimethylamino)propane sulfonate
CTAC - Cetyltrimethylammonium chloride
CTAB - Cetyltrimethylammonium bromide
DMABMN - N,N-dialkylaminobenzylidene malononitrile
DNSC - Dansyl chloride
ED AC - Ethyl p-dimethylamino cinnamate
HPBI - 2-(2'-hydroxyphenyl)benzimidazole
3-HF - 3-Hydroxyflavone
2-Methylandracene - 2-MeAn
NpOH - 2 - naphthol
Pe - Perylene
NPN - N-Phenylnaphthylamine
PVA - Poly(vinyl alcohol)
PPG - Poly(propylene glycol)
Py - Pyrene
PyCHO - Pyrene-3-carboxaldehyde
PyTS - 8-Hydroxy-1,3,6-pyrenetrisulfonate
PTC - 3, 4, 9, 10-Perylene tetracarboxylate
SDS - Sodium dodecyl Sulfate
SDU - 5(E)-Styryl-1,3-dimethyl uracil
TNS - 2-(p-Toluidinyl)-naphthalene-6-sulfonate
TX-100 - Triton X-100

1.6. References


