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PHOTOPHYSICAL PROCESSES IN ORGANIZED ASSEMBLIES

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Dynamics of different photophysical processes are markedly affected in organized media. Confinement of the probe in a small volume seriously hinders the free motion of the probes. The local properties such as, polarity, viscosity and *p*H in an organized media are very different from those in an ordinary liquid. The extreme sensitivity of the dynamics of the photophysical processes have been utilized to infer the microscopic properties of the organized media.

Key Words: Photophysical Processes; Photoisomerisation; Nanoenvironment; Micelles; Lipid Vesicles; Solvation Dynamics; Organized Assemblies

1 Introduction

Self-organized molecular assemblies play a major role in many natural and biological processes. The spontaneous formation of these assemblies particularly in aqueous medium is a result of the interplay between the very strong water-water interactions and the weak interaction among the organic molecules. In an organized assembly, the active chemical species remains confined in a small region, a few nm in size. Such confinement in a small volume imposes severe restrictions on the free motion of the probe and the confined solvent molecules. The 'local' properties e.g. polarity, viscosity and *p*H in such a nanoenvironment are often vastly different from those in a bulk medium. Chemical reactivity and dynamics in such a confined environment are vastly different from those in any homogeneous fluid medium due to the proximity and the favourable disposition of the confined reactants and the markedly altered local properties. Chemistry in organized media mimic the extremely efficient chemical processes occurring in the biological systems.[1-5] This provides the main impetus to study organized assemblies. Photophysical processes in organized assemblies are interesting particularly for two reasons. In the present review, we will discuss how rate of some of the photophysical processes change quite dramatically in organized assemblies and how this remarkable sensitivity can be utilized to probe the organized assemblies.

There are several types of organized molecular assemblies. Some of them are molecular aggregates formed in polar liquids (e.g. micelles in water) or nonpolar liquids (e.g. reverse micelles or micro-emulsions in hydrocarbons). Further examples include several cage like hosts soluble in many liquids (cyclodextrins or calixarenes), microporous solids (e.g. zeolites), and semirigid materials (e.g. polymers, hydrogels etc.) which can encapsulate suitably sized guest molecules.

The organization of the present review is as follows. In Section 2, we will give a general overview of several photophysical processes which are used as a probe for the organized assemblies. In Section 3, we will describe the architecture of some organized assemblies. Finally, in Section 4 we will discuss the recent results on the dynamics of various photophysical processes in these assemblies.

Photophysical processes in organized assemblies have been discussed in many recent reviews. In the volume edited by Ramamurthy, several authors summarized the progress in this area up to 1991.[1] Several authors have discussed the effect of cyclodextrins on many photophysical processes.[2] The hydrophobic effect, which causes binding of organic probes with cyclodextrins and other hosts in aqueous medium has been reviewed thoroughly.[3]

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Many organized assemblies involve an interface between two drastically different media. Chemical and physical processes at various interfaces have been recently studied using a number of new experimental and theoretical techniques.[4-5]

2 Photophysical Processes

In this Section, we will discuss the salient features of several photophysical processes. Due to our interest in the dynamics of the photophysical processes we will emphasize the factors which govern the dynamics of these processes.

Solvent Relaxation

Solvent relaxation refers to the reorientation of polar solvent molecules about a dipole instantaneously created in a polar solvent. For this purpose, one uses a solute which is non-polar or weakly polar in the ground state and is highly polar in the electronically excited state. A dipole can be created instantaneously by exciting such a probe with an ultrashort picosecond or femtosecond light pulse. When the probe solute is in the ground state, the polar solvent molecules remain randomly oriented around the non-polar or weakly polar probe solute molecule. Immediately after excitation by an ultrashort pulse, the polar solvent molecules remain randomly oriented around the dipole created as the solvent relaxation is very much slower than the excitation process. Subsequently, the solvent molecules gradually reorient around the newly created electron or dipole. This process of reorientation of the solvent dipoles around an electron or a dipole is referred to as the solvation dynamics. The system eventually reaches the fully solvated state. The solvation time, τ_s, is defined as the time taken for the solvent molecules in going from the randomly oriented configuration to the fully solvated state. As the solute dipole, in the excited state, is gradually stabilized through solvation, the incompletely solvated species decays rapidly giving rise to a fast decay at the blue end of the emission spectrum. The solvated species however, grows with time, and this growth is manifested at the red end of the emission spectrum. This results in the gradual decrease in the emission energy i.e. red shift of the emission spectra with increase in time. This phenomenon is known as the time dependent Stokes shift (TDSS).[6-7] The wavelength dependent temporal decays of emission and TDSS are regarded as the evidences of solvation dynamics. The TDSS technique is the most popular method of studying solvation dynamics. The solvation dynamics is followed by the decay of the solvent response function, $C(t)$, which is defined as,

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)}$$

where $\nu(0)$, $\nu(t)$ and $\nu(\infty)$ are the emission frequencies at time zero, t and infinity respectively. The solvation time, τ_s, is the time constant of the decay of the response function $C(t)$, so that $C(t)=\exp(-t/\tau_s)$. If the decay of $C(t)$ is multiexponential, e.g. $a_1\exp(-t/\tau_1)+a_1\exp(-t/\tau_2)$, one considers the average solvation time $<\tau_s>=a_1\tau_1+a_1\tau_2$. The solvation time is also known as the longitudinal relaxation time of the solvent. According to the simple continuum theory, the solvation time is related to the dielectric relaxation time, τ_D, as,[8-9]

$$\tau_s = (\varepsilon_\infty/\varepsilon_0)\ \tau_D$$

where ε_∞ and ε_0 are respectively the dielectric constants at high frequency and that at zero (static) frequency. For most polar liquids, $(\varepsilon_\infty/\varepsilon_0) < 1$. As a result the solvation time, τ_s is shorter than the dielectric relaxation time. It is obvious that solvation dynamics studies provide valuable information on the mobility of confined solvent molecules in an organized assembly. Since water is by far the most important solvent for the biological systems, in the next section, we will briefly discuss some recent results on solvation dynamics and dielectric relaxation in pure water.

Solvation Dynamics and Dielectric Relaxation in Water

For water, $\varepsilon_\infty \approx 5$, $\varepsilon_0 \approx 80$ and the dielectric relaxation time (τ_D)[12] is 10 ps. Thus, according to the simple continuum theory, the solvation time of water should be $\approx (5/80)\times 10$ or 0.6 ps. The first experimental study on the solvation dynamics of the water molecules around a dye molecule, coumarin 343, was performed by Barbara *et al.*[9] They reported solvation times of 0.16 ps and 1.2 ps with relative contributions of 1:2. Later using a set up with a better time resolution, Fleming *et al.*[9] detected an initial ultrafast Gaussian component $(a_g e^{-\frac{1}{2}\omega_g^2 t^2})$ with a frequency ω_g=38.5 ps^{-1} and a

slower biexponential decay with time constants of 126 fs and 880 fs, respectively. They assigned the ultrafast gaussian component to the intramolecular vibration and librational motions of the water molecules and the slower component, to their diffusive, reorientational motion. Using molecular hydrodynamic theory, Bagchi *et al.* discussed the role of different vibrational modes on the solvation dynamics in water and showed that the initial ultrafast part is controlled by the intramolecular vibration and the librational modes of water.[10] This model predicts a deuterium isotope effect at long time. Schwartz and Rossky later calculated a similar 20% isotope effect.[10]

While the properties of the water molecules in bulk have been studied quite thoroughly for a very long time, much less is known about the behaviour of water molecules in confined environments. There is considerable recent interest on the structure and dynamics of water molecules at various interfaces. Recent molecular dynamics simulations indicate that the dielectric constant of water decreases by as much as a factor of 16, when the water molecules are confined in a volume of dimension 27 Å.[13]

The dynamics of the so called "biological water" molecules, in the immediate vicinity of a protein, has been studied using various techniques. While the dielectric relaxation time of ordinary water molecules is 10 ps,[12] both the dielectric[14-16] and NMR relaxation studies,[17] indicate that near the protein surface the relaxation dynamics is bimodal with two components in the 10 ns and 10 ps time scale, respectively. The 10 ns relaxation time can not be due the motion of the peptide chains which occurs in the 100 ns time scale. From the study of NMR relaxation times of ^{17}O at the protein surface, Halle *et al.*[17] suggested a dynamic exchange between the slowly rotating internal and the fast external water molecules. To explain the bimodal dielectric relaxation in aqueous protein solutions, Nandi and Bagchi proposed a similar dynamic exchange between the "bound" and the free water molecules.[18] The "bound" water molecules are those which are attached to the biomolecule by strong hydrogen bonds. Their rotation is coupled with that of the biomolecule. The water molecules, beyond the solvation shell of the proteins, behave as free water molecules. The free water molecules rotate freely and contribute to the dielectric relaxation process, whereas the rotation of the doubly hydrogen-bonded "bound" water molecules is coupled with that of the biomolecule and hence, is much slower.

Using conjugate peak refinement method, Fischer *et al.*[19] calculated the reaction path of the motion of the biological water molecules. They also compared the computed transition state and activation energy to those in ice. Their calculation shows that the motion of the water molecules, buried in the proteins, involves exchange of two water hydrogen atoms and involves two successive rotations around orthogonal axes.

In a later section, we will show that the substantially slower dielectric relaxation times of water in organized assemblies, markedly slow down the solvation dynamics, in some cases by 4 orders of magnitude, compared to bulk water.

Photoisomerisation

In the ground state of a molecule *cis-trans* isomerisation i.e. rotation about an olefinic double bond is not allowed because it involves a very large barrier, roughly equal to the π-bond energy. However, the π-bond order becomes zero in the $\pi\pi^*$ excited state and thus, rotation about double bond and hence, *cis-trans* isomerisation is possible in the $\pi\pi^*$ excited state. The interconversion of different rotational and geometric isomers via the excited state is known as photoisomerisation. In the excited state, the system moves freely along the torsional coordinate. When it reaches the perpendicular geometry, it undergoes rapid transition from the excited electronic state to the nearly isoenergetic ground state. Once the system is at the peak of the barrier between the *cis* and the *trans* isomer in the ground state, it can go to either of them with equal probability, resulting in photoisomerisation.[20] The photoisomerisation plays an important role in many chemical and biological processes, which include the vision process. The vision process involves such a *cis-trans* photoisomerisation about the C_{11}-C_{12} double bond of a retinyl polyene attached to the opsin part of a 7-helix membrane protein, rhodopsin.[21-22]

The dynamics of the photoisomerisation process depends on the friction offered by the medium to the motion of the system along the torsional coordinate. In Kramers' seminal work,[23] the isomerisation process is viewed as a one dimensional barrier crossing and the rate constant k_{iso} is given by,

$$k_{iso} = \{[\zeta/2\omega_b I]^2 + 1\}^{1/2} - [\zeta/2\omega_b I],$$

where ζ, denotes the friction, ω_b, the barrier frequency and I is the moment of inertia. If the friction is purely hydrodyamic in nature,

$$\zeta = 4\pi\eta d r^2,$$

where η, is the bulk viscosity, d and r, are molecular dimensions associated with the isomerising groups. At very high viscosity, the Kramers' relation reduces to a simple relation where k_{iso} becomes inversely proportional to the viscosity of the medium. This is known as the Smoluchowski limit. The failure and success of the Kramers' theory has been the subject of intense debate. The failure of Kramers' theory is often ascribed to three factors. Firstly, the friction is often described incorrectly by the hydrodynamic model. There are several improved models, e.g. the time dependent friction model where the friction is assumed to be different at different parts of the potential barrier.[24] Secondly, for many probes (e.g. stilbene, diphenylbutadiene etc.) the isomerisation process is not strictly one dimensional. Thirdly, the microviscosity around a probe molecule may not be same as the bulk viscosity.[25-26] Several authors tried orientational relaxation time as an empirical parameter for microviscosity and found good correlation between the rate of isomerisation and that of orientational relaxation.[25]

According to the Kramers' expression the viscosity dependence of the isomerisation process is rather complicated. However, the relation becomes very simple at very high viscosity (i.e. Smoluchowski limit). Since many organized assemblies possess very high microviscosity it is reasonable to assume that the Smoluchowski limit is valid for them. We will demonstrate that assuming the Smoluchowski limit, the microviscosities of some organized assemblies can be estimated quite accurately.

For some probes, the activation barrier for the isomerisation process and hence, the isomerisation dynamics depends on the polarity of the media. For *trans*-stilbene, Hicks *et al.*[27] observed that the slope of the isoviscous plots of $\ln(k_{iso})$ against $1/T$ decreases with increase in the viscosity. Since for alcohols, higher viscosity is associated with lower polarity, Hicks *et al.*[27] proposed that the barrier for the isomerisation process, decreases at higher viscosity and hence, at lower polarity. However, for the cyanine dye DODCI, slopes of the isoviscous plots of $\ln(k_{iso})$ against $1/T$ in alcoholic solvents do not vary much with increase in viscosity.[28] This indicates that the photoisomerisation of DODCI is more or less unaffected by the polarity of the medium.[32] Waldeck *et al.*[20] showed that a barrier for the isomerisation process can be extracted only for solvents like nitriles where the solvent relaxation is much faster than the excited state isomerisation process. In slower solvents like alcohols, the slow and incomplete solvation obscures observation of a well-defined barrier for the isomerization process.

Excited State Proton Transfer

Acid-base properties of many molecules in the excited state differ considerably from those in the ground state.[27] For instance, aromatic amines are weakly basic in the ground state. But, many of them become acidic in the excited state and readily donate a proton to a proton-acceptor to produce the anion in the excited state. Such a molecule which behaves as an acid in the excited state, is called a photoacid and similarly photobases are those which display basic properties in the excited state. In many cases, excited state proton transfer (ESPT) results in dual emission bands. One of these emission bands arises from the neutral excited state and bears mirror image relation with the absorption spectrum. The other emission band is due to the excited deprotonated (anion) or protonated species and exhibits large Stokes shift. In an intermolecular proton transfer process, the proton is transferred from one molecule to another. In this case, the basic issues are whether the acid-base equilibrium is attained within the excited state lifetime of the photoacid or the photobase. If the acid-base equilibrium is attained in the excited state, excited state pk_a and pk_b are determined by steady state or time resolved emission spectroscopy. Ireland and Wyatt summarized the excited state pk_a and pk_b of many organic molecules.[29]

There have been several attempts to determine the exact number of solvent molecules, needed to solvate and stabilize the ejected proton.[30-36] It has been demonstrated that for proton transfer from 1-naphthol to protic solvents in ultracold solvent clusters in supersonic jet, 3 ammonia and 2 piperidine molecules are needed to solvate the ejected proton while for water clusters no proton transfer is observed in jets even for clusters containing 21 water molecules.[30] For liquid

solutions, Robinson *et al.* suggested that 4±1 water molecules are needed to solvate a proton to form a cluster $H^+(H_2O)_{4\pm1}$.[31] In an organized assembly the local pH is often very different from the bulk pH. Again, in an organized medium adequate number of water molecule (4±1) are often unavailable to solvate the ejected proton. As a result, the proton transfer processes in the organized assemblies differ considerably from those in the ordinary solutions.

ESPT is the main nonradiative pathway in the excited state of many biological probes. One of the most prominent among them is the popular DNA probe ethidium bromide (EB).[37-39] On addition of DNA, EB readily intercalates in the double helix of DNA in aqueous solutions.[37-38] The intercalation causes nearly 11 fold increase in the emission intensity and lifetime of EB. The fluorescence enhancement of EB on intercalation, is not due to high local viscosity as the emission quantum yield and lifetime of EB are very similar in methanol and glycerol, whose viscosity differ by a factor of 2000.[39] Emission intensity of EB is low in highly polar, protic solvents, such as alcohol and water, compared to polar, aprotic solvents, e.g., acetone or pyridine. It is proposed that water quenches emission of EB by abstracting the amino proton.[39] If this conjecture is correct, the emission intensity of EB should depend on the hydrogen bond acceptor (HBA) basicity of the solvent, β, instead of the polarity. The HBA basicity, β, introduced by Kamlet *et al.* and other polarity scales of various solvents are elaborately discussed in the literature.[40] Polarity of acetone (dielectric constant, $\varepsilon = 20.7$ and $E_T(30) = 42$) is less than that of another polar, aprotic solvent, acetonitrile ($\varepsilon = 37.5$ and $E_T(30) = 46$).[40] However, the HBA basicity, β, of acetone (0.48) is greater than that of acetonitrile (0.31) and thus, acetone is a better proton acceptor than acetonitrile. Pal *et al.*[41] observed that in the more polar but weaker proton acceptor, acetonitrile, the fluorescence intensity and lifetime of EB are 1.25±0.1 times those in acetone. This conclusively establishes that the high is HBA basicity of the solvent, the high is the nonradiative rates of EB, and hence, the low is the emission intensity. Thus the nonradiative rates of EB are controlled by the HBA basicity of the solvent rather than the solvent polarity. This lends further support to the contention that ESPT is the main nonradiative pathway for EB.

Twisted Intramolecular Charge Transfer

If an electron donor and an acceptor is joined by a flexible single bond, electronic excitation results initially a "nonpolar" excited state. Subsequently an intramolecular electron transfer occurs from the donor to the acceptor and simultaneously the donor and the acceptor undergo a twist about the flexible bond joining them. This process is known as twisted intramolecular charge transfer (TICT) and the resulting highly polar state is known as a TICT state. The TICT process often results in dual emission from the "nonpolar" and the TICT state.[42-43] This phenomenon was first proposed to explain the dual emission of *p*-dimethylamino benzonitrile (DMABN). Subsequently, this phenomenon is observed in many other systems. The relative energies of the TICT and LE state change markedly with solvent polarity. In a nonpolar solvent, the LE state remains lower in energy compared to the TICT state and hence, a single emission band due to the LE state is observed. In a polar solvent, the more polar TICT state becomes stabler than the LE state. This is manifested in the dual emission from the LE and TICT state. The solvent dependence of the TICT process has been investigated using several theoretical models.[43-45] Soblewski *et al.*[45] used CIS, CASSCF and CASPT2 methods to calculate the reaction path for the TICT process in DMABN and its analogues. Unlike earlier calculations which considered a single internal coordinate, Soblewski *et al.* took into account more than one internal coordinates.[45] Their calculation support the TICT hypothesis for DMABN. For DMABE, for which dual emission is not observed in a polar solvent like acetonitrile, they proposed strong quenching via the weakly fluorescent rehybridised-ICT state. The effect of polar solvents on the spectra of molecules undergoing TICT in supersonic jet has been studied by many groups. Most recently, Ishida *et al.*[46] studied the dynamics of the intramolecular charge transfer process in ultracold clusters of 9,9'-bianthryl with water in supersonic jet using picosecond time resolved spectroscopy. They observed that the LE state is converted to the unrelaxed CT state in a time scale of <20 ps. Following this, the unrelaxed CT state relaxes in 50 ps time scale to a new equilibrated state. The dynamics of the TICT process can be followed by the decay of the nonpolar emission and the rise in the TICT emission. The dynamics of the TICT

process depends strongly on the polarity of the medium. It has been proposed that the energy barrier for the TICT process for dimethylamino-benzonitrile (DMABN) decreases linearly with the polarity parameter $E_T(30)$[47] of the medium as

$E_B = E_B^0 - A\,[E_T(30)\text{-}30]$,

where E_B^0, is the barrier in a hydrocarbon medium of $E_T(30)$=30. The polarity dependent barrier model is subsequently extended to many other TICT probes.[43,48] In many cases, the TICT state is non-emissive and for them the TICT process is simply a nonradiative decay process in the "nonpolar" excited state of these molecules. The nonradiative rate is obtained from the emission quantum yield (ϕ_f) and lifetime (τ_f), as $k_{nr}=(1-\phi_f)/\tau_f$. The TICT rate is very much sensitive to the polarity of the medium. For instance, in the case of TNS, ϕ_f changes 300 times from 0.3 in dioxane ($E_T(30)$=36) to 0.001 in water ($E_T(30)$=63) and τ_f changes over 100 times from 8 ns in dioxane to 0.06 ns in water. Thus the rate constant of TICT is a very sensitive indicator of the microscopic polarity of an organized media and has been used quite extensively for this purpose.[43]

3 Organized Media

In this Section, we will discuss the architecture of a few organized media. Since structures of these organized media have already been discussed in a number of reviews we will present only a brief overview instead of giving a comprehensive summary.

Micelles

Amphiphilic surfactant molecules form spherical or nearly spherical aggregates called micelles, above a certain critical concentration, known as the critical micellar concentration (cmc) and above a critical temperature, called "Kraft temperature".[49] The size of the micellar aggregates is usually 1-10 nm and the aggregation number, i.e. the number of surfactant molecules per micelle, ranges from 20 to 200. The core of a micelle is essentially "dry" and consists of the hydrocarbon chains with the polar and charged head groups projecting outward into the bulk water. The core is surrounded by a polar shell, which is called the Stern layer for an ionic micelle and palisade layer for a neutral micelle. The Stern (palisade) layer comprises of the ionic or polar head groups, bound counter ions and water molecules. Between the Stern layer and the bulk water there is a diffuse layer, termed the Guoy-Chapman (GC) layer which contains the free counter ions and water molecules.

Detailed information on the structure of the micelles has recently been obtained through small angle X-ray and neutron scattering studies.[50] According to these studies, the thickness of the Stern layer is 6-9 Å for cationic cetyl trimethyl ammonium bromide (CTAB) micelles and anionic sodium dodecyl sulfate (SDS) micelles, whereas the palisade layer is about 20 Å thick for neutral triton X-100 (TX-100) micelles. Radius of the dry, hydrophobic core of TX-100 is 25-27 Å, and thus the overall radius of TX-100 micelle is about 51 Å. The overall radius of CTAB and SDS micelles are about 50 Å and 30 Å, respectively.

Telgmann and Kaatze studied the structure and dynamics of micelles using ultrasonic absorption in the 100 KHz to 2 GHz frequency range.[51] They detected several relaxation times in the long (μs), intermediate (10 ns) and fast (0.1-0.3 ns) time scale. The longest relaxation time has been attributed to the exchange of monomer between the bulk and the micelles while the fastest to the rotation of the alkyl chains of the surfactants in the core of the micelle. The intermediate relaxation time has not been assigned to any particular motion. We will discuss later that the intermediate relaxation times in the 10 ns time scale may well be due to the solvent relaxation in the Stern layer.

Reverse Micelles and Microemulsions

The reverse micelles refer to the aggregates of surfactants formed in non-polar solvents, in which the polar head groups of the surfactants point inward while the hydrocarbon chains project outward into the nonpolar solvent.[52-58] Their cmc depends on the non-polar solvent used. The cmc of aerosol-OT (sodium dioctyl sulfosuccinate, AOT), in a hydrocarbon solvent is about 0.1 mM.[52] The AOT reverse micelle is fairly monodisperse with aggregation number around 20 and is spherical with a hydrodynamic radius of 1.5 nm.

The most important property of the reverse micelles is their ability to encapsulate fairly large amount of water to form what is known as a "microemulsion". Up to 50 water molecules, per molecule of the surfactant, can be incorporated inside the AOT reverse micelles. Such a surfactant-coated nanometer-sized water droplet, dispersed in

a nonpolar liquid, is called a "water pool". The radius (r_w) of the water pool varies linearly with the water to surfactant mole ratio, w_0. In *n*-heptane, r_w (in Å) $\approx 2w_0$.[53] The structural information on the microemulsions i.e. radius of the micellar aggregates and that of the water pool has been obtained using dynamic light scattering,[57] transient grating, ultrasound velocity measurements,[55] FT-IR,[56] dielectric relaxation[58] etc. Several non-ionic or neutral surfactant, (e.g. triton X-100, etc) have recently been reported to form reverse micelles in pure and mixed hydrocarbon solvents.[59] Finally, apart from water, confinement of other polar solvents such as, acetonitrile, alcohol and formamide, have been reported in such microemulsions.[60]

The water molecules confined in the water pool of the microemulsions differ in a number of ways from ordinary water. In a microemulsion, the first 2-4 water molecules are very tightly held by the surfactant and all the water molecules except the 6 most tightly held ones freeze at -50^0C. The FT-IR[56] and the compressibility studies[55] indicate that the first three water molecules "lubricate" the dry surfactants. During this process the compressibility of the AOT microemulsion increases steeply. The next three water molecules solvate the counterion (Na^+ for Na-AOT) and starts the self-organization process. At this stage, the head groups of AOT become linked by hydrogen bonds through the water molecules and the compressibility gradually decreases. For $w_0>6$, the water pool swells in size but the compressibility reaches a plateau. Around $w_0=13$, the first solvation shell of AOT becomes complete and up to this point, the water structure remain severely perturbed inside the water pool. But even in the very large water pools, the compressibility of the microemulsions remains at least two times higher than that of ordinary water.[55] Behaviour of the microemulsions containing neutral surfactants are similar except that they exhibit only a monotonic increase of compressibility reaching a plateau and does not show the decrease of compressibility observed for the ionic surfactants arising from the solvation of the counter ions. In the water pool, there may be three kinds of water molecules, the "bound" ones near the polar head group of the surfactant and hence, held strongly, the "free" ones near the central region of the water pool and the "trapped" ones between the surfactants. Using FT-IR spectroscopy, Jain *et al.*[56] determined the relative amounts of the three kinds of water molecules. Obviously, the "free" water molecules expected to be faster than "bound" ones. In the solvation dynamics experiments to be are discussed later, it will be seen that even the "free" water molecules, in the water pools, are significantly slower than ordinary water molecules.

Dielectric relaxation studies have revealed a component of 7 ns in the microemulsions which suggest significant retardation of the motion of the confined water molecules in the water pool.[58]

Lipid Vesicles

Vesicles are basically a water pool entirely enclosed by a membrane which is basically a bilayer of the lipid molecules which are dispersed in aqueous medium.[61-69] For an unilamellar vesicle there is only one such bilayer while a multilamellar vesicle (radius ~1000 nm) consists of several concentric bilayers. Unilamellar vesicles can be produced by breaking the multilamellar vesicles by sonication. In such a system there are two kinds of water molecules present, those in the bulk and those entrapped within the water pool of the vesicles. The entrapped water pool of a small unilamellar DMPC vesicle is much bigger (radius ≈250 nm) than those of the water pool of the reverse micelles (radius < 10 nm). In recent years, several groups studied chain dynamics of lipids using SANS, ESR of spin-labelled lipids and fluorescence of pyrene-labelled lipids.[61] Recent molecular dynamics (MD) simulations,[63] crystal structure[64] and other studies indicate that above transition temperature (≈23°C) each DMPC molecule is hydrogen bonded to about 4.5 water molecules which form an inner hydration shell of the polar head group of the lipids and about 70% of the DMPC molecules remain connected by the water bridges.

The vesicles undergo phase transition at a well-defined temperature. Above the phase transition temperature, the viscosity of the lipid bilayer remains quite low and the permeability of the bilayer wall remains high so that small molecules easily pass through the bilayer to enter the inner water pool. Below the transition temperature, viscosity of the lipid bilayer becomes high and also the permeability across the bilayer membrane decreases significantly. The change in the viscosity of the lipid bilayers with temperature is usually monitored by optical anistropy studies. The

transport of small organic molecules across the lipid bilayer above transition temperature is most elegantly demonstrated in a recent surface second harmonic (SSH) generation study by Srivastava and Eisenthal.[69] The SSH signal is obtained as long as the molecule stays in an inhomogeneous region i.e. at the lipid bilayer. Above the transition temperature of the lipids, the SSH signal decays in a time scale of 100 seconds which denote the residency time of the probe in the bilayer or the time taken by the probe to diffuse through the bilayer membrane from bulk water to the inner water pool. For lipids below the transition temperature no such time dependence of the SSH signal is observed which indicates that at a temperature below the transition temperature the bilayer membrane does not allow transport of molecules to the inner water pool.

Polymers and Hydrogels

Water soluble polymers and the microporous synthetic polymer hydrogels, have generated considerable recent interest because of their versatile applications and compatibility with biological systems.[70-80] The hydrogels are inherently insoluble in water but can entrap considerable amount of water within their polymer networks.[76-77] They have versatile applications as biomaterials (e.g. contact lenses), chromatographic packings, in devices for controlled-release of drugs, and as electrophoresis gels. The polyacrylamide (PAA) hydrogel is obtained by polymerising acrylamide in the presence of N,N′-methylene bisacrylamide as a crosslinker.[78] The pore size in such a gel can be varied by varying the concentration of the monomer (acrylamide).[76] Among the various types of hydrogels PAA is most suitable for photophysical studies as it is optically transparent over a wide range of concentrations of the monomer and the cross-linker. On absorption of water such a hydrogel swells in size. The swelling and other properties of this interesting semirigid material has recently been studied using light scattering,[74] NMR and calorimetry.[79] The bulk viscosity of any hydrogel is very high. However, since the hydrogels contain large pores even very large biological macromolecules like DNA pass through such hydrogels during gel electrophoresis. Several groups attempted to immobilise small probe molecules (e.g. nile red)[80] within the hydrogels. Using far field fluorescence microscopy Moerner *et al.* demonstrated that in PAA hydrogel while most nile red molecules move freely, motion of a minute fraction (~2%) of them becomes severely restricted so that the Brownian motion of *individual* nile red molecules may be recorded.[80]

Zeolites

Zeolites are open structures of silica in which some of the silicon atoms in the tetrahedral sites are replaced by aluminium ions.[81-83] Counterions like Na^+, K^+ maintain the electroneutrality and reside freely inside certain locations in the zeolite cages. Zeolites can be represented by the empirical formula $M_{2/n}Al_2O_3.\ xSiO_2.\ yH_2O$, where M is an alkali metal or an alkaline earth metal cation of valence n, $x>2$ and y varies from 0 to 10. Depending on the Si/Al ratio and the cations, zeolites can have various rigid and well defined structures which can be classified into cage and channel types. For the ZSM-5 zeolite, there are two intersecting channel systems. One system consists of straight channels with a free cross-section of 5.4×5.6 Å^2 and the other consists of sinusoidal channels with free diameter of 5.1×5.5 Å^2. Faujasite zeolites are made up of a nearly spherical supercage of diameter 13 Å, surrounded by sodalite cages.

The structure and dynamics of zeolites have been studied by molecular dynamics (MD) simulation, Monte Carlo simulation, density functional theory and stochastic models.[83,89] These studies indicate that the spatial locations are similar for different cations. The mobile cations are responsible for the electrical conductivity of dehydrated zeolites. The mechanism of electrical conduction in a zeolite has been the subject of several studies. Conduction of dehydrated potassium zeolite L has been found to involve a thermally activated process. Dielectric properties of the zeolites depend on the degree of hydration. The zeolites can act as a host for a large number of guest molecules. Neutron diffraction study suggests that in zeolite Y, cyclohexane stays in the 12-ring window site. This is in agreement with the MD simulations. Similar results are obtained for benzene in zeolites.[88] NMR line width and simulation studies indicate that in the faujasite zeolites the guest aromatic molecules hop from one cage to another in the nanosecond time scale.[89]

The photophysics and photochemistry of organic molecules change remarkably on encapsulation in

zeolite.[81] The marked changes caused by the zeolites result partly from their rigid structure which imposes considerable restriction on molecular motion within a zeolite. Secondly, the presence of cations in close proximity with organic guest molecules exert significant influences because of the strong local electric field produced by the cations and also the enhanced singlet-triplet transitions in the case of zeolites having heavy cations. The polarity and acid-base behaviour of the zeolites also affect different photophysical processes.

4 Photophysical Processes in Organized Assemblies

In this Section, we will discuss how the dynamics of various photophysical processes are modified inside organized assemblies. Since the dynamics of the photophysical processes depends on the microscopic property (polarity, viscosity etc.) of the medium, the photophysical studies reveal information on the microscopic property of the organized assemblies.

Solvation Dynamics in Organized Assemblies

The solvation dynamics depends on the mobility of the solvent molecules in a medium. Due to the importance of water in biological systems we will focus our attention on relaxation properties of water in organized assemblies. The dielectric relaxation studies have already indicated that the water molecules present in biological environments are substantially slower compared to ordinary water. We will now show that the solvation dynamics studies, also reveal similar trends and reveal more direct information on mobility of water molecules in organized media.

Cyclodextrin

Cyclodextrins are water soluble cyclic polysaccharides which conatin a hydrophobic cavity of height 8 Å and diameter 5-8 Å in which organic molecules bind readily in aqueous medium. Fleming *et al.*[90] studied solvation dynamics of two laser dyes, coumarin 480 (C480) and coumarin 460 (C460) in γ-cyclodextrin (γ-CD) cavity. The marked blue shift of the emission spectra and the increase in fluorescence lifetimes of the two probes on addition of γ-CD to their aqueous solutions indicate that the probes are located inside the γ-CD cavity.[91] The initial component of solvation in γ-CD is found to be similar to that in bulk water (0.31 ps).[90] However, at longer times, the solvent response in γ-CD, reveal a component which is at least three orders of magnitude slower. Molecular dynamics calculations indicate that in the γ-CD cavity there are 13 water molecules for C480/γ-CD complexes and 16 in the case of C460.[90] Since these numbers resemble the number of water molecules present in the first solvent shell of the dyes in aqueous solutions, the response at short times for the C480/γ-CD complex should have been different from that for C460 due to the presence of fewer water molecules for the former. However, as the initial Gaussian component is same for the two dye molecules, it appears that the first solvent shell does not dominates the solvent response.[90]

Nandi and Bagchi[92] showed that the slow solvation dynamics in γ-CD may be explained if one assumes complete freezing of the translational motions of the solvent molecules inside the γ-CD cavity. They further showed that the slow part of the response contributes about 10% to the total response. It is proposed that the collective response of the solvent molecules, rather than the contribution from the different solvent shells, dominates the inertial component of solvation.

Microemulsion

The surfactant-coated water droplets in water-in-oil microemulsions serve as excellent model for the water molecules in confined environments. The emission spectra of certain solvent sensitive probes change markedly when it is transferred from bulk hydrocarbon to the water pool of a microemulsion. For example, absorption maximum of coumarin 480 (C480) in *n*-heptane and water are at 360 nm and 395 nm, respectively while the corresponding emission maxima are at 410 nm and 490 nm, respectively.[93] In a *n*-heptane solution of C-480 on addition of AOT and subsequently water, a very prominent shoulder appears at 480 nm (Fig. 8).[94] The 480 nm emission band and having excitation peak at 390 nm is assigned to the C480 molecules in the water pool of the microemulsion. Sarkar *et al.* studied the solvation dynamics of C480 in AOT/*n*-heptane/water microemulsions.[94] They observed distinct rise time in the nanosecond time scale at the red end of the emission spectra. This indicates nanosecond solvation dynamics in the microemulsions. They observed that in a small

water pool (w_o=4, r_w=8Å) the solvation time is 8 ns while for a very large water pool (w_o=32, r_w= 64Å) the response is bimodal with a fast component of 1.7 ns and a slower component of 12 ns. For acrylodan-labelled human serum albumin in AOT microemulsion, using phase fluorimetry Bright *et al.* reported that the solvation time is about 8 ns for a small water pool (w_o=2) and 2 ns for a large water pool (w_o=8). For 4-aminophthalimide (4-AP), in a large water pool, the solvation dynamics is biexponential with an average solvation time of 1.9 ns.[96] In AOT microemulsions, the solvation time of 4-AP increases from 1.9 ns in H_2O to 2.3 ns in D_2O, which displays a 20% deuterium isotope effect. The appearance of a nearly 2 ns component in the large water pools indicates that even in the large water pools of the microemulsions the water molecules are about 6000 times slower compared to bulk water (solvation time 0.31 ps[90]).

A semi-quantitative explanation of the 2 ns component may be as follows. The static polarity or the dielectric constant of the water pool of the AOT microemulsions can be obtained from the position of the emission maximum of the probes (C480 and 4-AP).[94-96] For both the probes the water pool resembles an alcohol like environment with an effective dielectric constant ≈30-40. The dielectric relaxation time in such a water pool is about 10 ns.[58] If one makes a reasonable assumption that the infinite frequency dielectric constant of water in the water pool of the microemulsions is same as that of ordinary water i.e. 5, then the solvent relaxation time should be about 1.67 ns which is close to the observed solvation time in AOT microemulsions.

One might argue that the nanosecond dynamics observed in the water pool is not due to the slower water molecules but is because of the solvation by the Na^+ counter ions present in the water pool for the AOT microemulsions. Nanosecond solvation dynamics due to ions, in solutions as well as molten salts, is well documented in the literature.[97-99] Mandal *et al.*[100] studied the solvation dynamics of 4-AP in a microemulsion containing neutral surfactant triton X-100 where no ions are present in the water pool. The triton X-100 microemulsion also exhibits nanosecond solvation dynamics which suggests that the ionic solvation dynamics has little or no role in the solvation dynamics observed in the water pool.

Levinger *et al.* studied the solvation dynamics of a charged dye coumarin 343 (C343) in lecithin[101] and AOT microemulsions[102-103] using femtosecond upconversion. For lecthin microemulsions,[103] the solvent relaxation displays a very long component which does not become complete within 477 ps. This observation is similar to the nanosecond dynamics reported by Bright *et al.*[95] and Sarkar *et al.*[94] For C343 in AOT, Levinger *et al.* observed that the decay characteristics of the emission intensity at different wavelengths display considerable differences for sodium and ammonium counterions.[102] They however, did not present a complete analysis of this result in terms of dynamic Stokes shift and the decay of the solvent response function C(t). For Na-AOT, the solvation dynamics reported by Levinger *et al.*[103] for the charged probe C343 is faster than that reported by Bright *et al.*[95] and Sarkar *et al.*[94] It is obvious that due to its inherent negative charge, AOT repel the negatively charged C343 probe from its vicinity. Thus the C343 anion is expected to reside in the central region of the water pool. Neutral probes like C480 and 4-AP may stay both in the central region of the pool as well as in the peripheral region close to the AOT molecules. The discrepancy in the results in the case of AOT microemulsions, reported by Levinger *et al.* and those of Sarkar *et al.* and Bright *et al.* however, is too large to be explained in terms of different locations of the probes and merits further careful investigation.

Most recently, several groups studied solvation dynamics of nonaqueous solvents, such as, formamide,[103] acetonitrile and methanol[104] in AOT microemulsions. Using a picosecond setup, Shirota and Horie[104] demonstrated that in the AOT microemulsions the solvation dynamics of acetonitrile and methanol is non-exponential and 1000 times slower compared to those in the pure solvents. They attributed the non-exponenial decay to the inherent inhomogeneous nature of the solvent pools. Evidently, the static polarity and relaxation properties of the entrapped polar solvents vary quite strongly as a function of the distance from the ionic head group of the AOT surfactants. Within its nanosecond excited lifetime, the probe passes through different layers of solvents of different relaxation properties within the pool. This quite reasonably may give rise to a non-exponential decay.

Micelles

In aqueous micellar solutions, there are three possible locations of the probe, namely the bulk water, the "dry" micellar core and the Stern layer. Obviously the solvation time will be in the sub-picosecond time scale in the bulk water. In the dry hydrocarbon core of the micelle the probe is not expected to exhibit dynamic Stokes shift. However, if the probe stays in the Stern layer, its solvation dynamics may be quite different from that in the bulk water because the mobility of the water molecules may be considerably constrained in the Stern layer. Solvation dynamics in micelles has been studied using C480 and 4-AP as probes.[105-106] Emission properties of the probes in the micelles, are very different from those in water and in hydrocarbon. This shows that the probes reside neither in bulk water nor in core of the micelles and hence, are located in the Stern layer of the micelles. Sarkar *et al.*[105] and Datta *et al.*[106] studied solvation dynamics of C480 and 4-AP, respectively, in neutral (TX-100), cationic (CTAB) and anionic (SDS) micelles. It is observed that for SDS, CTAB, and TX-100, the average solvation times are respectively 180 ps, 470 ps and 1450 ps for C480[105] and 80, 270 and 720 ps for 4-AP.[106] The solvation times in micelles, differ only by a factor of 2 for the two probes. This suggests that the solvation dynamics in the Stern layer of the micelles does not depend very strongly on the probe. It is interesting to note that the time scale of solvation is similar to the intermediate range of dielectric relaxation times reported by Telgmann and Kaatze.[51] It is readily seen that the solvation dynamics in the Stern layer of the micelles is 3 orders of magnitude slower than that in bulk water (0.31 ps[90]), about 10 times faster than that in the water pool of the microemulsions,[94-96] and is slightly faster than the longest component of solvation dynamics in γ-CD.[90] The main candidates causing solvation in the Stern layer of the micelles, are the polar or ionic head groups of the surfactants, the counter ions (for SDS and CTAB) and the water molecules. Since the head groups are tethered to the long alkyl chains their mobility is considerably restricted. The dynamics of such long alkyl chains occurs in the 100 ns time scale[61] and hence, is too slow to account for the subnano-second solvation dynamics observed in the micelles. The role of ionic solvation by the counter ions also appears to be minor because of the very similar time scale of the ionic (CTAB) and the neutral (TX-100) micelles.

Lipids

The state of solvation of a fluorescent probe, in the ground state, in the unilamellar and multilamellar vesicles is usually studied by the red edge excitation spectroscopy (REES).[67] The dynamics of the surfactant chain in the lipid bilayer is usually investigated using optical anisotropy and ESR.[61] However, the interesting issue of the dynamics of the water molecules inside the water pool of vesicles has been addressed only recently.[107] Datta *et al.*[107] studied C480 in sonicated unilamellar DMPC vesicles. The position of emission maximum of C480 in DMPC vesicles is once again different from that in bulk water and the hydrocarbon. This indicates the probe stays in the inner water pool of the vesicle. Datta *et al.*[107] observed that the solvation dynamics of C480 in DMPC vesicles is highly nonexponential with two components of 0.6 ns (40%) and 11 ns (60%). This result is very similar to the solvation dynamics of the same probe in the large water pools of AOT microemulsions.[94] Thus the nanosecond solvation dynamics in lipids can not be due to the chain dynamics of DMPC which occurs in the 100 ns time scale.[61] Since in the bulk water the solvation dynamics is much faster (0.31 ps[90]) the results reported by Datta *et al.*[107] demonstrates restricted motion of the water molecules in the inner water pool of the vesicles.

Polymer Hydrogels

Due to the bulk viscosity of the polymer solutions and particularly the semirigid hydrogels, one expects very slow relaxation of the water molecules in polymer matrices and polymer hydrogels. Contrary to this expectation, in the orthosilicate[108] and polyacrylamide[109] hydrogels, both solvation dynamics and rotational relaxation are found to occur in <50 ps time scale. The surprisingly fast solvation and rotational dynamics of small probe molecules in hydrogels may be attributed to the porous structure of the hydrogels, through which even large biomolecules pass through easily. Datta *et al.*[109] demonstrated that the microenvironment of 4-AP in polyacrylamide (PAA) hydrogel is quite heterogeneous. In the PAA hydrogel, there are broadly two kinds of environments. One of them is water like in which

the 4-AP molecules exhibits emission maximum at 550 nm with lifetime 1.3 ns and the other is quite aprotic in which 4-AP emits at 470 nm with a 7.2 ns lifetime. The recent steady state anisotropy measurements by Claudia-Marchi *et al.*[110] demonstrates that for titania gels at the sol-gel transition point when the bulk viscosity increases abruptly, the emission anisotropy does not change perceptibly. Thus the microviscosity of the gel is very low in spite of the very high bulk viscosity. The NMR[111] and simulation[112] studies indicate that the diffusion coefficient of water molecules in polymer hydrogels is not appreciably slower compared to ordinary water and is smaller at most by a factor of 2 than that in ordinary water. Argaman and Huppert[113] studied solvation dynamics of coumarin 153 in polyethers and found very fast solvation times ranging from 50 fs to 100 ps. The fast solvation dynamics in polymer matrices is consistent with the dielectric relaxation studies[72] which shows that except the highly water soluble polymer, polyvinyl pyrolidone, dielectric relaxation times of most aqueous polymer solutions is faster than the 100 ps time scale.

Liquid Crystal

In search of the pseudonematic domains having long range order several groups have recently studied solvation dynamics in the nematic phase of the liquid crystals.[114-115] Rhodamine 700[114] and coumarin 503[115] exhibit biexponential solvation dynamics in liquid crystals. For coumarin 503 the slowest time constant decreases from 1670 ps at 311.5 K to 230 ps at 373 K. The solvation time is not affected by the nematic-isotropic phase transition. Thus, it appears that the local environment and not the long range order, controls the time dependent Stokes shift.

Zeolite and Nanoparticles

The solvation dynamics in microporous solids has been the subject of some recent studies. Sarkar *et al.*[116] showed that C480 exhibits wavelength dependent decays and time dependent Stokes shift in a solid host, faujasite zeolite 13X. They observed a highly non-exponential decay with an average solvation time of 8 ns. Interestingly the 8 ns time constant is very close to the nanosecond solvation dynamics ($\langle\tau\rangle$=4.1 ns) observed in molten salts.[97] In a faujasite zeolite the mobile components are the sodium ions and the probe dye molecule, itself. Since in a faujasite zeolite the encapsulated guest molecules hop from one cage to another in the nanosecond timescale,[89] the 8 ns relaxation time observed in zeolite may also arise as a result of the self-motion of the probe from one cage to another. The role of self-motion of solutes on the solvation dynamics has recently been discussed in detail by Biswas and Bagchi.[117] However, it is difficult to establish unequivocally whether the nanosecond dynamics observed in zeolite is due to ionic solvation or self-motion of the probe.

Pant and Levinger[118] studied solvation dynamics of C343 in a suspension of nanodimensional zirconia particles of radius 2 nm, in water-acetone mixture (95:5, v/v). They observed two subpicosecond components similar to those in bulk but having different amplitudes resulting in a relaxation time faster than that in bulk solution. They also showed that the maximum Stokes shift is three times smaller for the dye molecules adsorbed on the zirconia particles compared to those in bulk solution.

Proteins and DNA

One of the longstanding goals of biology is to understand the dynamics occurring in complex biomolecules such as proteins and DNA.[119-120] Several groups reported that the solvation dynamics of protein bound fluorophores is significantly slower compared to bulk water. Pierce and Boxer[121] and Bashkin *et al.*[122] reported that the solvation dynamics in the protein environments is non-exponential with a long component with time constant on the order of 10 ns. It is interesting to note that this time scale is very close to the nanosecond component of dielectric relaxation earlier observed for the aqueous protein solutions.[14-15,18]

The static and dynamic properties of DNA have been studied by the temperature dependent Stokes shift of an intercalated dye, acridine orange[123]. A large part of the Stokes shift of the intercalated dye in DNA, is found to be frozen out at low temperature, as in the solution. Thus, the interior of DNA is found to have the diffusive and viscous dynamic characteristics of a fluid, rather than the purely vibrational characteristics of a crystal. The results suggest that the probe dye molecule senses the movement of DNA and at high viscosity, the rate of DNA motion is limited by the rate of solvent motion.

Photoisomerisation and Microviscosities of Organized Assemblies

The friction imparted by several organized assemblies and interfaces to the photoisomerisation of organic molecules has been the subject of several recent studies. The rate of photoisomerisation of stilbene, in various organized assemblies is substantially slower compared to that in a homogeneous medium. Lifetime of *trans*-stilbene increases from 34 ps in aqueous methanol to 137 ps in aqueous solution of α-cyclodextrin (α-CD). This indicates that isomerisation of stilbene inside α-CD cavity is slower than that in aqueous methanol.[124] In the bigger β- or γ-CD cavity, fluorescence decays of *trans*-stilbene are biexponential with one component of 50 ps and another very slow component of several thousand picosecond. The slow component corresponds to a very rigid microenvironment.[124] In a zeolite, isomerisation of stilbene is retarded so much that its rate becomes comparable to the rate of intersystem crossing. This results in a strong phosphorescence.[125] Holmes *et al.* observed a biexponential decay for stilbene in a lipid and assigned this to the presence of two sites.[126] The isomerisation of 3,3'-diethyloxadicarbocyanine iodide (DODCI) and other cynaine dyes and malachite green (MG) has been studied at various interfaces, such as the air-water interface,[5] microemulsions,[127] micelles,[128] DNA and proteins.[129] The recent time resolved surface second harmonic generation (SSHG) experiments have demonstrated that for the air-water interface, the friction against the photoisomerisation is different for different probes.[5] While, for rod shaped DODCI, the isomerisation at the air-water interface is faster compared to that in the bulk water, for nearly planar malachite green, it is slower at the air-water interface.[5] In the water pool of a microemulsion, photoisomerisation of DODCI is nearly three times slower compared to ordinary water.[127] The photoisomerisation of DODCI is markedly slowed down at various micelle-water interfaces.[128] Compared to aqueous solution, in CTAB, SDS and TX-100 micelles, the rates of photoisomerisation of DODCI are respectively. 20, 7 and 8 times slower. It is pointed out earlier that at very high viscosity, the rate of photoisomerisation becomes inversely proportional to the viscosity of the medium (Smoluchowski limit). Assuming that the Smoluchowski limit and the same "slip/stick" boundary condition hold for the highly viscous solvent, *n*-decanol and the micelles and then, comparing the isomerisation rates of DODCI in the three micelles with that in *n*-decanol, the microviscosities of CTAB, SDS and TX-100 have been estimated to be 70.0±20, 24.5±2 and 26.0±2 cP, respectively.[128] Photoisomerisation of DODCI is also studied in aqueous solution in the presence of salmon sperm DNA and bovine serum albumin (BSA).[129] It is observed that the microenvironments of aqueous solutions of DNA and BSA behave like a highly viscous liquid and result in completely suppression of the isomerisation process.

Due to the very high local viscosity in the organized assemblies, the torsional motion of the TPM dyes is significantly hindered resulting in a dramatic increase in the quantum yield and lifetime of emission of the TPM dyes compared to aqueous solutions. Baptista and Indig[130] reported a 1000 fold increase in the quantum yield and lifetime of emission of TPM dyes on binding to a protein BSA. This suggests that the local viscosity of the protein is several orders of magnitude higher compared to that of water. Tamai *et al.*[131] studied the microviscosities of the polyacryamide gels using TPM leuco dyes. The microviscosity of the unswollen and the swollen gels has been esimated to about 20 cP and 10 cP respectively. This once again demonstrates that while the bulk viscosity of the semirigid gels is many thousand times higher than that of water, the microviscosity is only 10-20 times higher. This is consistent with the very fast solvation and rotational relaxation time in gels reported earlier.[108-109]

Proton Transfer Processes in Organized Assemblies

The pK_a of an acid and hydrogen ion concentration in an organized assembly often differ drastically from those in ordinary liquids. Measurement of the *p*H at a surface is one of the longstanding goals in chemistry. Using absorption spectra of bromophenol indicators, Mukherjee and Banerjee[132] estimated the *p*H and pK_a at the micelle-water interface. Eisenthal *et al.* used surface second harmonic generation to determine surface *p*H, pK_a and potential (ψ) at the air-water interface.[5] The results depend strongly on the nature of charge of the surfactants. For instance, if the surfactant is negatively charged (e.g. *p*-alkyl phenolate) the hydrogen ion concentration at the surface is greater than that in the bulk while the

opposite is true for a cationic surfactant (e.g. *p*-alkyl anilinium).[5]

In AOT microemulsions, presence of the negatively charged head group causes a sharp gradient in *p*H/pOH over the nanometer sized water pool. Menger and Saito[133] reported that the acid-base property of *p*-nitrophenol (PNP) gets substantially modified in AOT microemulsions. While in bulk water, at *p*H=11.5, 95% of the PNP molecules remain in the anionic form, when an alkaline aqueous solution containing PNP is injected in the AOT microemulsion, no *p*-nitrophenolate anion is detected until the *p*H of the injected solution exceeds 11.5. On the basis of this, Menger and Saito concluded that the pK_a of PNP, in the AOT microemulsion, is greater than that in bulk water (7.14) by more than 4 units. However, it has been pointed out later that the local hydroxyl ion concentration near the negatively charged AOT head group, is substantially less than that in bulk water. Oldfield *et al.*[134] showed that if a negatively charged group is attached to PNP, the probe remains in the water pool of the AOT microemulsions and its acid-base property is similar to that in bulk water. Okazaki and Toriyama[135] studied the location of an organic acid at different *p*H in AOT microemulsion, using ESR spectroscopy. They observed that at low *p*H, when the molecule is in the neutral form, it stays close to the AOT-water interface, while at high *p*H the carboxylate anion is expelled from the AOT-water interface to the water pool.

The dynamics of the excited state proton transfer processes in organized assemblies are often quite different from those in ordinary solutions.[136] The sharp local variation of *p*H in the water pool of the AOT microemulsions affects the intermolecular proton transfer process quite strongly. Fendler *et al.*[137] studied excited state deprotonation of a tri-negatively charged probe, hydroxypyrene-trisulfonate in AOT microemulsions. They observed that while in the large pools the proton transfer process is similar to that in bulk water, it is quite different in the small water pools (w_0<7). They concluded that in the large water pool, due to the electrostatic repulsion from the negatively charged AOT ions, the negatively charged probe remains in the large water pools, far from the AOT anion and experiences an almost bulk water-like microenvironment. But in the small water pool, the very different local *p*H, near the AOT anions, renders the deprotonation/reprotonation behaviour quite different from that in ordinary aqueous solutions. In ordinary aqueous solutions emission of ethidium bromide (EB), EB is strongly quenched by the hydroxyl ions. However, in AOT microemulsion, the hydroxyl ion does not quench the EB emission at all even when a highly alkaline aqueous solution of EB (*p*H=12.6) is injected into the reverse micelle.[41] It is proposed that the anionic surfactant, AOT, strongly attracts the ethidium cation to the AOT-water interface, but expels the hydroxyl anion from the AOT-water interface to the water pool and hence, the hydroxyl anion can not access the ethidium cation.[41]

Fleming *et al.*[138] reported that the deprotonation rate of 1-naphthol is retarded 20 times inside cyclodextrin cavities, while deprotonation of protonated aminopyrene occurs nearly 3 times faster. Since in water-alcohol mixture, deprotonation rate for protonated aminopyrene, increases with alcohol concentration up to about 65-70% and decreases at higher alcohol concentrations,[32] the faster deprotonation of protonated aminopyrene, inside the cyclodextrin cavity, indicates that the polarity of the microenvironment is in between pure water and 65% alcohol. For 1-naphthol, the deprotonation rate monotonically decreases as the alcohol content increases.[34] The slower deprotonation rate of 1-naphthol in cyclodextrin[138] is consistent with this. Mandal *et al.*[139] reported dramatic reduction in the rate of excited state deprotonation of 1-naphthol in micelles, from 35 ps in bulk water to the nanosecond time scale. The retardation of the rate of proton transfer of 1-naphthol is manifested in the dramatic enhancement of the neutral emission at 360 nm. Along with this there is marked increase in the lifetime of the neutral emission at 360 nm and the rise time of the anion emission (460 nm), for CTAB, SDS and TX-100R. For cationic CTAB, the rise time of the anion emission (600 ± 100 ps) is similar to the lifetime of decay at 360 nm. However, for TX-100R and SDS, the rise time of the anion emission (at 460 nm) is found to be faster than the decay of the neutral emission (at 360 nm). This indicates that in TX-100R and SDS, there is no parental relation between the normal and the anion emission and they originate from the probe, 1-naphthol molecules, at distinctly different locations. This is consistent with the earlier observation,[34] that in alcohol-water mixtures at

high alcohol content the rise time of the anion emission is faster than the decay time of the neutral form. For TX-100R and SDS, the rise times of the 460 nm band are 1.8±0.1 ns and 600±100 ps, respectively. The corresponding decay times at 360 nm are 2.5±0.1 ns and 1.8±0.1 ns, respectively.[139] The dramatic reduction in the rate of deprotonation of 1-naphthol in micelles is attributed to the non-availability of adequate number of water molecules to solvate the proton in the micellar environment. The ESPT process of 1-naphthol is also affected by lipids and found to report faithfully the transition temperature of the lipids.[140]

TICT and Micropolarity of the Organized Assemblies

Since the dynamics of the twisted intramolecular charge transfer (TICT) process is very sensitive to the polarity of the medium, the microscopic polarity of an organized medium may be determined from the rate of the TICT process. For TNS, which is nearly nonfluorescent in water (ϕ_f=10^{-3} and τ_f=60 ps), the emission quantum yield and life time increases nearly 50 times on binding to cyclodextrins and more than 500 times on binding to a neutral micelle, triton-X 100 (TX).[43] Such a dramatic increase in the emission intensity and lifetime arises because of the marked reduction of the nonradiative TICT process inside the less polar microenvironment of the cyclodextrins and the micelle. Determination of the micropolarities of various organized assemblies using TICT probes, has been surveyed quite extensively in several recent reveiws.[43] Therefore, in this article we will focus only on some selected works not covered in the earlier reviews.

Inside the water pool of the microemulsions of the TICT process of several probes (ANS,[141] TNS,[142] nile red[143] etc.) is observed to be significantly retarded compared to bulk water and the lifetime of the probes increase from the picosecond time scale in water to several nanosecond in the water pool. The retardation of the TICT process inside the water pool of the microemulsion compared to ordinary water, is ascribed to the lower static polarity of the water pool compared to bulk water. The polarity or $E_T(30)$ of the pool is obtained from the observed rate of TICT and comparing them with the values obtained in homogeneous solutions. Karukstis *et al.* analyzed the emission spectra of PRODAN in microemulsions and showed that the PRODAN molecules at different sites within the microemulsions exhibit different emission spectra.[144] More recently, using picosecond total internal reflection, Bessho *et al.*[145] determined the emission lifetime of ANS at the water-heptane interface. The observed a nanosecond component in the decay of ANS at the water-heptane interface which indicates that the interface is considerably less polar than bulk water.

The polarity of the supercages of solid faujasite zeolites has been estimated using TICT probes. For this purpose, Ramamurthy *et al.*[146] used DMABN and Sarkar *et al.*[147] used nile red as the probe. Both the studies indicate that the polarity of the faujasite zeolite resembles that of 1:1 methanol-water mixture. Kim *et al.*[148] studied TICT of dimethyl-amino-benzoic acid (DMABA) in faujasite Y zeolites. In Y zeolites the lifetime of the TICT emission and the TICT/LE emission intensity ratio of DMABA are greater than those in polar solvents. This is attributed to hydrogen bonding between DMABA and the zeolites. Kim *et al.*[149] studied the effect of neutral SiO_2 colloids of diameters 300-400 Å in acetonitrile, on the dual emission of DMABA. For 10 μM DMABA, they found that up to a concentration of 0.3 μM SiO_2 the intensity of the TICT band increases while that of the normal band (LE) decreases. Intensity of the TICT emission decreases at SiO_2 concentrations above 0.3 μM. They attributed this to the formation of hydrogen bond between the SiO_2 particles and the DMABA molecule. At high SiO_2 concentrations due to submonolayer coverage of the silica particles the TICT emission decreases.

The internal cavity of the cyclic polysaccharide, cyclodextrin (CD) is highly nonpolar and hydrophobic and is known to retard the TICT process markedly when the probe gets encapsulated inside the cavity.[2,43] More recently, a linear polysaccharides dextrin has also been reported to provide a hydrophobic surface to which the probe TNS binds due to hydrophobic effect and as a result of lower local polarity, the TICT rate is retarded nearly 50 times[150]. The effect of salting in (urea, $LiClO_4$ etc.) and salting out (LiCl) agents on the hydrophobic binding of TNS with dextrin has been studied in detail. Interestingly another linear polysaccharide, dextran affect the emission properties of TNS, vary slightly. This is attributed to the difference in the stereochemistry of dextrin

and dextran. For dextrin, one surface is highly polar with all the hydroxyl groups of the sugar pointing outward from it, while the other surface is completely devoid of hydroxyl group and hence, is nonpolar and hydrophobic. For dextran both the surfaces contain hydroxyl groups and hence, are polar.

Kim *et al.* studied effect of cyclodextrin (CD) on the emission properties of DMABA in aqueous solutions and reported that α-CD enhances the nonpolar (LE) emission and β-CD enhances the TICT emission[151]. Matsushita and Hikida[152] studied the effect of α-CD on the emission properties of p-dimethylamino acetophenone (DMACP) in aqueous solutions. DMACP does not give TICT emission in aqueous solutions. However on addition of α-CD both the LE and TICT emission of DMACP is enhanced. To explain the larger enhancement of the LE emission they proposed a 1:2 complex in which the DMACP molecule is completely enclosed by two α-CD molecules.

The extraordinary sensitivity of the TICT probe, TNS, has recently been exploited to probe the interaction of cyclodextrins (CD) and surfactants.[153] Study of such interactions is important due to the potential application of CD in targeted drug delivery, and particularly for understanding how CD affects cell membrane surfactants. The important issues are whether CD preserves the structure of the membranes and releases the drug encapsulated inside its cavity. Critical micellar concentration (cmc) of several ionic surfactants (alkyl sulfates, sulfonates and tetra-alkyl ammonium halides) as well as neutral surfactants (Triton X-100, Igepal etc.), have been reported to increase on addition of CD, while their aggregation numbers remain more or less unchanged.[154-157] The emission quantum yield of TNS in TX-100 micelles is nearly 10 times that of TNS bound to CD-s while the lifetime of the micelle bound TNS is about 5 times higher. On addition of TX-100 to an aqueous solution containing CD, the emission intensity of TNS initially exhibits a slight decrease and beyond a particular concentration of TX-100, the emission intensity and lifetime of TNS increase abruptly. The point of abrupt increase of emission intensity and lifetime of TNS, gives the apparent cmc of TX-100 in the presence of CD. The apparent cmc of TX-100 increases significantly on addition of β-CD. In 10 mM β-CD, the apparent cmc of TX-100 is 7.25 ±0.25 mM. This is 28±1 times the cmc of TX-100 in water.[240] However, in the presence of α-CD at similar concentrations, cmc of TX-100 remains more or less unaffected.[153] This indicates that TX-100 molecules bind very strongly with the large β-CD and very weakly with the small α-CD. This is in sharp contrast to the behaviour of the linear surfactants for which both α-CD and β-CD cause an increase in cmc. The dramatic difference in the interaction of TX-100 with α- and β-CD, may be attributed to the difference in size between α- and β-CD. Due to its large size the TX-100 molecule can not be inserted in the small α-CD cavity and thus addition of α-CD leaves the cmc of TX-100 unchanged. TX-100 however, is easily accommodated in the bigger β-CD cavity and thus is rendered unavailable for the formation of the micelles causing an increase in the cmc. The initial decrease in the emission intensity of TNS, at TX-100 concentrations below the apparent cmc, is ascribed to the competitive binding of TNS and TX-100 with β-CD. This causes displacement of TNS from the CD cavity by the TX-100 surfactant molecules. The binding constant of TX-100 with β-CD is estimated to be 9400 ±1300 L M^{-1}.

5 Conclusion

It is apparent that the dynamics of various photophysical processes are markedly modified in the organized assemblies and are thus sensitive probes to study the microscopic properties of the organized assemblies. Perhaps the most significant result is the observation that the water molecules in different organized and biological assemblies are significantly slower than ordinary water molecules. It is demonstrated that the local polarity, *p*H and viscosity in an organized media are markedly different from those in the ordinary solutions and often vary quite drastically over a small distance. Ultrafast lasers and the various sophisticated theoretical models which revolutionized chemical dynamics in ordinary liquids in the eighties, have been applied to study organized assemblies only recently and still the field is largely unexplored. Though the inherent complexity of the organized assemblies still eludes a complete and quantitative understanding of some of the questions there has been a significant improvement in our understanding of various issues. The enhanced

understanding about the structure and function of organized assemblies should enable us to mimic the natural systems more closely.

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References

1 *Photochemistry in Organized and Constrained Media* (Ed.(V Ramamurthy) VCH New York (1991)
2 V T D'Souza and K B Lipkowitcz *Chem Rev* **98** (1998) 1741; P Bortulos and S Monti *Adv Photochem* **21** (1995) 1; K A Konnors *Chem Rev* **97** (1997) 1325; G Wenz *Ange Chem Int Ed Engl* **34** (1994) 741; I M Warner *Anal Chem* **70** (1998) 477R
3 R Breslow *Chem Rev* **98** (1998) 1997; W Blokzijl and J B F N Engberts *Angew Chem Int Ed Engl* **32** (1993) 1545
4 R B Miranda and Y R Shen *J Phys Chem B* **103** (1999) 3292; I Benjamin *Annu Rev Phys Chem* **48** (1997) 401
5 K B Eisenthal *Chem Rev* **96** (1996) 1343
6 G R Fleming and M Cho *Annu Rev Phys Chem* **47** (1996) 109; R M Stratt *Acc Chem Res* **28** (1995) 201; P J Rossky and J D Simon *Nature* **369** (1994) 471
7 M L Horng, J A Gardecki and M Maroncelli *J Phys Chem A* **101** (1997) 1030
8 B Bagchi and R Biswas *Acc Chem Res* **31** (1998) 181; B Bagchi and N Gayathri A. *Adv Chem Phys* **89** (1998) 1
9 W Jarjeba, G C Walker, A E Johnson, N A Kahlow, and P F Barbara *J Phys Chem* **92** (1988) 7039; R Jimenez, G R Fleming, P V Kumar, M Maroncelli *Nature* **370** (1994) 263; C Silva, P K Walhout, K Yokoyama and P F Barbara *Phys Rev Lett* **80** (1998) 1086
10 N Nandi, S Roy and B Bagchi *J Chem Phys* **102** (1995) 1390; B J Schwartz and P J Rossky *J Chem Phys* **105** (1996) 6997
11 A J Benigno, E Ahmed and M Berg *J Chem Phys* **104** (1996) 7382
12 U Kaatze *Chem Phys Lett* **203** (1993) 1
13 L Zhang, H T Davies, D M Kroll and H S White *J Phys Chem* **99** (1995) 2878
14 R Pethig *Protein-Solvent Interactions* (Ed. R B Gregory) Marcel Dekker Inc. NY (1995) .265
15 S Mashimo, S Kuwabara, S Yagihara and K Higasi *J Phys Chem* **91** (1987) 6337
16 P S Belton *J Phys Chem* **99** (1995) 17061
17 V P Denisov, J Peters, H D Horlein and B Halle *Nature Struct Biol* **3** (1996) 505
18 N Nandi and B Bagchi *J Phys Chem B* **101** (1997) 10954; N Nandi and B Bagchi *J Phys Chem A* **102** (1998) 8217
19 S Fischer, C S Verma and R Hubbard *J Phys Chem B* **102** (1998) 1797
20 D H Waldeck *Chem Rev* **91** (1991) 415
21 S H Lin, M Groesbeck, I van der Hoef, P Verdegen, J Lugtenberg, R A Mathies *J Phys Chem B* **102** (1998) 2787
22 S Takeuchi and T Tahara *J Phys Chem A* **101** (1997) 3052
23 H A Kramers *Physica (The Hague)* **7** (1940) 284; P Hanggi, T Talkner and M Borkovec *Rev Mod Phys* **62** (1990) 251
24 B Bagchi and D W Oxtoby *J Chem Phys* **78** (1983) 2735; G Rothenberger, D K Negus and R M Hochstrasser *J Chem Phys* **79** (1983) 215
25 R M Bowman, D P Miller and K B Eisenthal *Chem Phys Lett* **155** (1989) 99
26 Y P Sun and J Saltiel *J Phys Chem* **93** (1989) 8310
27 J M Hicks, M T Vandersall, E V Sitzman, K B Eisenthal *Chem Phys Lett* **135** (1987) 413
28 S P Velsko and G R Fleming *Chem Phys* **65** (1982) 59
29 A Weller *Prog React Kinetics* **1** (1961) 188; J F Ireland and P A Wyatt *Prog Phys Org Chem* **12** (1976) 131
30 S K Kim, J J Breen, D M Willberg, L W Peng, A Heikal and A H Zewail *J Phys Chem* **99** (1995) 7421; A Douhal, F Lahmani and A H Zewail *Chem Phys* **207** (1996) 477
31 G W Robinson, P S Thistlewaite and J Lee *J Phys Chem* **90** (1986) 4224
32 E Pines and G R Fleming *J Phys Chem* **95** (1991) 10448
33 S P Webb, S W Yeh, L A Philips, M A Tolbert and J H Clark *J Am Chem Soc* **106** (1984) 7286
34 J Lee, G W Robinson, S P Webb, L A Philips and J H Clark *J Am Chem Soc* **108** (1986) 6538
35 J Lee, G W Robinson, S P Webb, L A Philips and J H Clark *J Am Chem Soc* **112** (1990) 1353
36 E Pines, D Huppert and N Agmon *J Chem Phys* **88** (1988) 5620
37 B H Robinson and G P Drobny *Ann Rev Biophys Biomol Struct* **24** (1995) 523; C V Kumar (ref. 1, p 783)
38 D P Millar, R J Robbins and A H Zewail *J Chem Phys* **76** (1982) 2080
39 J Ohmstead III and D R Kearns *Biochemistry* **16** (1977) 3647
40 M J Kamlet, J L M Abbouid and R W Taft *Prog Phys Org Chem* **13** (1981) 485; C Reichardt *Chem Rev* **94** (1994) 2319
41 S K Pal, D Mandal and K Bhattacharyya *J Phys Chem B* **102** (1998) 11017
42 Z R Grabowski *Pure Appl Chem* **65** (1993) 1751
43 K Bhattacharyya and M Chowdhury *Chem Rev* **93** (1993) 507
44 H J Kim and J T Hynes *J Photochem Photobiol A* **105** (1997) 337
45 A L Sobolewski, W Sudholt and W Domcke *J Phys Chem A* **102** (1998) 2716
46 T Ishida, Y Fujimura, T Fujiwara and O Kajimoto *Chem Phys Lett* **288** (1998) 433
47 J M Hicks, M T Vandersall, Z Babarogic and K B Eisenthal *Chem Phys Lett* **116** (1985) 18
48 Y Chang, P Chong and J D Simon *J Phys Chem* **99** (1995) 7382

49 D Attwood and A T Florence *Surfactant Systems* Chapman & Hall London (1983)
50 H H Paradies *J Phys Chem* **84** (1980) 599; S S Berr *J Phys Chem* **91** (1987) 4760; S S Berr, M J Coleman, R R M Jones and J S Johnson *J Phys Chem* **90** (1986) 5766; S S Berr, E Caponetti, R R M Jones, J S Johnson and L J Magid *J Phys Chem* **90** (1986) 5766
51 T Telgmann and U Kaatze *J Phys Chem A* **102** (1998) 7758 and 7766
52 Y C Jean and J H Ache *J Am Chem Soc* **100** (1978) 984 6320
53 J Eastoe, W K Young and B H Robinson *J Chem Soc Faraday Trans* **86** (1990) 2883
54 Y N Cao, H X Chen, G J Diebold, T Sun and M B Zimmt *J Phys Chem B* **101** (1997) 3005
55 A Amararene, M Gindre, J Y Le Huerou, C Nicot, W Urbach and M Waks *J Phys Chem B* **101** (1997) 10751
56 M B Temsamani, M Maeck, I El Hassani and H D Hurwitz *J Phys Chem B* **102** (1998) 3335; T De and A Maitra *Adv Coll Int Sci* **59** (1995) 95; T K Jain, M Varshney and A Maitra *J Phys Chem* **93** (1989) 7409
57 S P Moulik and B K Pal *Adv Coll Int Sci* **78** (1998) 99; K Mukherjee, D C Mukherjee and S P Moulik *Langmuir* **9** (1993) 1727
58 M D'Angelo, D Fioretto, G Onori, L Palmieri and A Santucci *Phys Rev E* **54** (1996) 993, 4620
59 D M Zhu, W Wu and Z A Schelly *J Phys Chem* **96** (1992) 2382, 712; H Caldaru, A Caragheorgheopal, M Dimonie, D Donescu, I Dragutan and N Marinescu *J Phys Chem* **96** (1992) 7109
60 R E Riter, J R Kimmel, E P Undiks and N Levinger *J Phys Chem B* **101** (1997) 8292
61 R Cassol, M T Ge, A Ferrarini and J H Freed *J Phys Chem B* **101** (1997) 8782
62 M M Sung-Suh and L Kevan *J Phys Chem A* **101** (1997) 1414
63 M Pasenkiewicz-Gierula, V Takaoka, H Miyagawa, K Kitamura and A Kusumi *J Phys Chem A* **101** (1997) 3677
64 R M Pearson and I Pascher *Nature* **81** (1979) 499
65 *Liposomes: A Practical Approach* (Ed. R C New) Oxford University Press England (1990)
66 J R Lakowicz and S Keating-Nakamoto *Biochemistry* **23** (1984) 3013
67 A P Demchenko and A S Ladokhin *Eur Biophys J* **15** (1988) 569; A Chattopadhyay and S Mukherjee *Biochemistry* **32** (1993) 3804
68 K H de Haas, C Blom, D van den Ende, M H G Devits, B Haveman and J Mellema *Langmuir* **13** (1997) 6658
69 A Srivastava and K B Eisenthal *Chem Phys Lett* **292** (1998) 345
70 E Kumacheva, Y Rharbi, R Mitchel, M A Winnik, L Guo, K C Tam and R D Jenkins *Langmuir* **13** (1997) 182
71 A R Eckert, T J Martin and S E Webber *J Phys Chem A* **101** (1997) 1646
72 N Shiyanishiki, S Yagihara, I Arita and S Mashimo *J Phys Chem B* **102**, (1998) 3249
73 R Olender and A Nitzan *J Chem Phys* **102** (1995) 7180
74 L Bromberg, A Y Grossberg, Y Suzuki and T Tanaka *J Chem Phys* **106** (1997) 2906; I Ohmine and T Tanaka *J Chem Phys* **77** (1982) 8725
75 Y B Zhang and Y X Zhang *Macromolecules* **29** (1996) 2494
76 A Chrambach and D Rodbard *Science* **172** (1971) 440
77 A M Mathur, S K Moorjani and A B Scranton *J Macromol Science -Rev Macromol Chem Phys* **C36** (1996) 405
78 V F Janas, F Rodriguez and C Cohen *Macromolecules* **13** (1980) 977
79 H Walderhans and B Nystrom *J Phys Chem B* **101** (1997) 1524; A K Lele, M M Hirve, M V Badiger and R A Mashelkar *Macromolecules* **30** (1997) 157
80 R M Dickson, D J Norris, Y L Tzeng and W E Moerner *Science* **274** (1996) 966
81 V Ramamurthy, D F Eaton and J V Casper *Acc Chem Res* **25** (1992) 299; V Ramamurthy (ref 1 p 303)
82 V Lachet, A Boutin, B Tavitian and A H Fuchs *J Phys Chem B* **102** (1998) 9224
83 P Demontis and G B Suffriti *Chem Rev* **97** (1997) 2845
84 B Smit and T L M Maesen *Nature* **374** (1995) 42
85 L Campana, A Selloni and A Goursot *J Phys Chem B* **101** (1997) 9932
86 W E Farneth and R J Gorte *Chem Rev* **95** (1995) 615
87 P A Anderson, A R Armstrong, A Porch, P P Edwards and L J Woodball *J Phys Chem B* **101** (1997) 9892
88 G Vitale, C F Mellot, M Bull and A K Cheetham *J Phys Chem B* **101** (1997) 4559
89 G Schrimp, B Tavitian and D Espinat *J Phys Chem* **99** (1995) 10932
90 S Vajda, R Jimenez, S J Rosenthal, V Fidler, G R Fleming and E W Castner Jr *J Chem Soc Faraday Trans* **91** (1995) 867
91 A Nag, T Chakrabarty and K Bhattacharyya *J Phys Chem* **94** (1990) 4203; W R Bergmark, A Davies, C York and G Jones II *J Phys Chem* **94** (1990) 4203
92 N Nandi and B Bagchi *J Phys Chem* **100** (1996) 13914
93 G Jones II, W P Jackson and C Y Choi *J Phys Chem* **89** (1985) 294
94 N Sarkar, K Das, S Das, A Datta and K Bhattacharyya *J Phys Chem* **100** (1996) 10523
95 J S Lundgren, M P Heitz and F V Bright *Anal Chem* **67** (1995) 3775
96 S Das, A Datta and K Bhattacharyya *J Phys Chem A* **101** (1997) 3299
97 E Bart, A Melstein and D Huppert *J Phys Chem* **99** (1995) 99, 9253
98 E Neria and A Nitzan *J Chem Phys* **100** (1994) 3855
99 A Chandra, D Wei and G N Pattey *J Chem Phys* **98** (1993) 4959
100 D Mandal, A Datta, S K Pal and K Bhattacharyya *J Phys Chem B* **102** (1998) 9070
101 D M Willard, R E Riter and N E Levinger *J Am Chem Soc* **120** (1998) 4151
102 R E Riter, E P Undiks and N E Levinger *J Am Chem Soc* **120** (1998) 6062
103 R E Riter, D M Willard and N E Levinger *J Phys Chem B* **102** (1998) 2705; R E Riter, E P Undiks, J R Kimel, D D Pant and N E Levinger *J Phys Chem B* **102** (1998) 7931
104 H Shirota and K Horie *J Phys Chem B* **103** (1999) 1437
105 N Sarkar, A Datta, S Das and K Bhattacharyya *J Phys Chem* **100** (1996) 15483
106 A Datta, D Mandal, S K Pal and K Bhattacharyya *J Mol Liq* **77** (1998) 121
107 A Datta, S K Pal, D Mandal and K Bhattacharyya *J Phys Chem B* **102** (1998) 6114

108 J D Jordan, R A Dunbar and F V Bright *Anal Chem* **67** (1995) 2436
109 A Datta, S Das, D Mandal, S K Pal and K Bhattacharyya *Langmuir* **13** (1997) 6922
110 M Claudia-Marchi, S A Bilmes and R Negri *Langmuir* **13** (1997) 3655
111 T P Hsu, D S Ma and C Cohen *Polymer* **24** (1983) 1273
112 P A Netz and T Dorfmuller *J Phys Chem B* **102** (1998) 4875
113 R Argaman and D Huppert *J Phys Chem A* **102** (1998) 6215
114 J Rau, C Ferrante, F W Deeg and C Brauchle *J Phys Chem B* **103** (1999) 931
115 G Saielli, A Polomeno, P L Nordio, P Bertolini, M Ricci and R Righini *J Chem Soc Faraday Trans* **94** (1998) 121
116 K Das, N Sarkar, S Das, A Datta and K Bhattacharyya *Chem Phys Lett* **249** (1998) 323
117 R Biswas and B Bagchi *J Phys Chem* **100** (1996) 4261
118 D Pant and N E Levinger *Chem Phys Lett* **292** (1996) 200
119 R B McGregor and G Weber *Nature* **319** (1986) 70
120 J R Lakowicz *Principles of Fluorescence Spectroscopy* Plenum Press New York (1983) Chap. 8
121 D W Pierce and S G Boxer *J Phys Chem* **96** (1992) 5560
122 J S Baskhin, G McLendon, S Mukamel and J Marohn *J Phys Chem* **94** (1990) 4757
123 E B Brauns, C J Murphy and M Berg *J Am Chem Soc* **120** (1998) 2449
124 G L Duveneck, E V Sitzmann, K B Eisenthal and N J Turro *J Phys Chem* **93** (1989) 7166
125 V Ramamurthy, J V Casper and D R Corbin *Tet Lett* **31** (1990) 1097
126 A S Holmes, D J S Birch, A Sanderson and G G Aloisi *Chem Phys Lett* **266** (1997) 309
127 A Datta, S K Pal, D Mandal and K Bhattacharyya *Chem Phys Lett* **278** (1997) 77
128 S K Pal, A Datta, D Mandal and K Bhattacharyya *Chem Phys Let* **288** (1998) 793
129 D Mandal, S K Pal, A Datta and K Bhattacharyya *Res Chem Intermediates* **25** (1999) 685
130 M S Baptista and J L Indig *J Phys Chem B* **102** (1998) 4678
131 N Tamai, M Ishikawa, N Kitamura and H Masuhara *Chem Phys Lett* **184** (1991) 398
132 P Mukerjee and K Banerjee *J Phys Chem* **68** (1964) 3567
133 F M Menger and G Saito *J Am Chem Soc* **100** (1978) 4376
134 C Oldfield, B H Robinson and R B Freedman *J Chem Soc Faraday Trans* **86** (1990) 833
135 M Okazaki and K Toriyama *J Phys Chem* **93** (1989) 5027
136 V Ramamurthy and D F Eaton *Acc Chem Res* **21** (1988) 300
137 M J Politi, O Brandt and J H Fendler *J Phys Chem* **89** (1985) 2345
138 J E Hansen, E Pines and G R Fleming *J Phys Chem* **96** (1992) 6904
139 D Mandal, S K Pal and K Bhattacharyya *J Phys Chem A* **102** (1998) 9710
140 J Sujatha and A K Mishra *Langmuir* **14** (1998) 2256
141 C H Cho, M Chung, J Lee, T Nguyen, S Singh, M Vedamuthu, S Yao, S Bzhu and G W Robinson *J Phys Chem* **99** (1995) 7806
142 D Mandal, S K Pal, A Datta and K Bhattacharyya *Analytical Sciences* **14** (1998) 199
143 A Datta, D Mandal, S K Pal and K Bhattacharyya *J Phys Chem B* **101** (1997) 10221
144 K K Karukstis, A Frazier, C L Loftus and A S Tuan *J Phys Chem B* **102** (1998) 8163
145 K Bessho, T Uchida, A Yamauchi, T Shiyoa and N Teramae *Chem Phys Lett* **264** (1997) 381
146 V Ramamurthy, D R Sanderson and D F Eaton *Photochem Photobiol* **56** (1992) 251
147 N Sarkar, K Das, D N Nath and K Bhattacharyya *Langmuir* **10** (1994) 326
148 Y Kim, B I Lee and M Yoon *Chem Phys Lett* **286** (1998) 466
149 Y Kim, H W Cheon, M Yoon, N W Song and D Kim *Chem Phys Lett* **264** (1997) 673
150 K Das, N Sarkar, S Das, K Bhattacharyya and D Balasubramanian *Langmuir* **11** (1995) 2410
151 Y H Kim, D W Cho, M Yoon and D Kim *J Phys Chem* **100** (1996) 15670
152 Y Matshushita and T Hikida *Chem Phys Lett* **290** (1998) 349
153 S K Pal, A Datta, D Mandal, S Das and K Bhattacharyya *J Chem Soc Faraday Trans* **94** (1998) 3471
154 G G Gaitano, A Crespo, A Compostizo and G Tardajos *J Phys Chem B* **101** (1997) 4413
155 D J Jobe, V C Reinsborough and S D Wetmore *Langmuir* **11** (1995) 2476
156 G Nelson and I M Warner *Carbohydrate Res* **192** (1989) 305
157 V K Smith, T T Ndou, A Munoz de la Pena, I M Warner *J Inclu Phenomena & Mol Recog* **10** (1991) 471