STUDY OF ORGANIZED ASSEMBLIES AND SURFACES USING PICOSECOND LASERS

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Abstract –Dynamics of many ultrafast processes are markedly slowed down in various organized molecular assemblies compared to ordinary liquids. We will show that the solvation dynamics of water molecules is affected most dramatically and is retarded by 3-4 orders of magnitude in microemulsions, micelles and lipids. We will also discuss how the access to fewer water molecules and the drastically altered local pH in an organized assembly affects the excited state proton transfer processes. Finally, we will show how surface second harmonic generation can be used to study the air-water surface.

INTRODUCTION

In nature, self-organized molecular assemblies play a crucial role in many chemical and biological processes. In an organized assembly the local or microscopic properties (*e.g.* polarity, viscosity or pH) of a small region are often vastly different from those in the bulk. Confinement of a chemical species in such a small region of dimension a few nm brings about drastic changes of its structure, dynamics and reactivity.[1-3] Study of such organized assemblies is of fundamental importance to understand and mimic the complex natural and biological assemblies. In the present article we will briefly discuss the marked influence of the various organized assemblies on the dynamics of several ultrafast processes. Perhaps the most important issue is the relaxation of the water molecules in confined and biological environments.[4-8] Dielectric relaxation time of water is 10 ps.[5] However the recent dielectric relaxation[6] and NMR studies[6-7] indicate a nearly 1000 fold retardation of the relaxation dynamics of water in organized media. We will examine the effect of the slower dielectric relaxation time in organized assemblies on solvation dynamics. Proton transfer processes depend on the availability of adequate number of water molecules to solvate the ejected proton and the local pH/pOH. In an organized assembly the local pH/pOH is often very different from the bulk and adequate number of water molecules are often not available and as a result the excited state proton transfer processes are affected markedly. We will also discuss some recent applications of the novel surface second harmonic generation technique to study the air-water surface.

ORGANIZED ASSEMBLIES

In this section we will briefly outline the structural features of a few organized assemblies.

a) Micelles: The micelles are the nearly spherical aggregates of surfactant molecules formed in water or other highly polar and protic solvents formed at a concentration higher than a critical concentration, known as the critical micellar concentration (CMC). According to the small angle x-ray and neutron scattering studies, the core of the micelles are essentially "dry" and consists of the hydrocarbon chains with the polar and charged head groups projecting outward into the bulk water.[9-11] 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 (or palisade) layer comprises of the ionic or polar head groups, bound counter ions and water molecules. Thickness of the Stern layer is 6-9 Å for the 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. The overall radius of TX-100, CTAB and SDS micelles are about 50 Å, 50 Å and 30 Å, respectively. Recently Telgmann and Kaatze studied the structure and dynamics of micelles using ultrasonic absorption and detected several relaxation times in the long (μs), intermediate (10 ns) and fast (0.1-0.3 ns) time scale.[12] We will discuss later that the 10 ns relaxation time may be due to the solvent relaxation in the Stern or Palisade layer.

b) *Reverse micelles and microemulsions*: The reverse micelles are aggregates of surfactants formed in nonpolar solvents, with the polar head groups of the surfactants pointing inward and the hydrocarbon chains project outward into the nonpolar solvent. 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".[13-18] Up to 50 water molecules, per molecule of the surfactant, can be incorporated inside the AOT (sodium dioctyl sulfosuccinate) 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 increases with the water to surfactant mole ratio, w_0. For AOT in n-heptane, r_w (in Å) $\approx 2w_0$.[14] 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°C. The compressibility studies indicate that the first three water molecules "lubricate" the dry surfactants.[15] The next three water molecules solvate the counterion (Na^+ for Na-AOT) and starts the self-organization process. 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. Dielectric relaxation studies reveal a component of 7 ns in the microemulsions which suggest significant retardation of the motion of the water molecules in the water pool.[18]

c) *Cyclodextrins:* Cyclodextrins (CD-s) are cyclic polymers of α-amylose.[1] The are called α-, β-, and γ- according as they contain 6, 7 or 8 α-amylose units. The stereochemistry of CD molecules are such that the interior of the cavity is completely devoid of the hydroxyl group and hence, is hydrophobic. The height of the cavity is about 8 Å and the diameters are 4.5, 6.5 and 8 Å for α-, β-, and γ-CD. The CD-s are water soluble. In aqueous solutions organic molecules of suitable size bind to the CD cavity due to hydrophobic effect.[1,3] Confinement of the guest organic molecule in the small, hydrophobic and relatively nonpolar CD-cavity modify remarkably their dynamics and reactivity.

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 provide 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 more direct information on mobility of water molecules in organized media.

a) *Cyclodextrin:* Fleming *et al.* studied solvation dynamics of two laser dyes, coumarin 480 (C-480) and coumarin 460 (C-460) in γ-cyclodextrin (γ-CD) cavity.[19] The initial component of solvation in γ-CD is found to be similar to that in bulk water (0.31 ps). However, at longer times, the solvent response in γ-CD, exhibits a component which is at least three orders of magnitude slower. Nandi and Bagchi 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.[20] They further showed that the slow part of the response contributes about 10% to the total response.

b) *Microemulsion:* The surfactant-coated water droplets in water-in-oil microemulsions are excellent models for the water molecules in confined environments. The emission spectra of certain solvent sensitive probes change markedly when they are transferred from bulk hydrocarbon to the water pool of a microemulsion. For example, absorption maximum of coumarin 480 (C-480) 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.[21] In a n-heptane solution of C-480 on addition of AOT and subsequently water, a very prominent shoulder appears at 480 nm.[22] The 480 nm emission band having excitation peak at 390 nm is assigned to the C-480 molecules in the water pool of the microemulsion. Sarkar *et al.* studied the solvation dynamics of C-480 in AOT/n-heptane/water microemulsions.[22] They observed distinct rise time in the nanosecond time scale at the red end of the emission spectra. This indicates solvation dynamics in the nanosecond time scale in the microemulsions. They observed that in a small water pool ($w_0=4$, $r_w=8$ Å) the solvation time is 8 ns while for a very large water pool ($w_0=32$, $r_w=64$ Å) the response is bimodal with a fast component of 1.7 ns and a slower component of 12 ns. For acrylodan-labeled 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 ($w_0=2$) and 2 ns for a large water pool ($w_0=8$).[23] For 4-aminophthalimide (4-AP), in a large water pool, the solvation dynamics is biexponential with an average solvation time of 1.9 ns for H_2O and 2.3 ns for D_2O, which displays a 20% deuterium isotope effect.[24] 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).

A semi-quantitative explanation of the 2 ns component may be as follows. For both the probes (C-480 and 4-AP), the water pool resembles an alcohol like environment with an effective static dielectric constant, (ε_0) 30-40.[22,24] The dielectric relaxation time (τ_D) in such a water pool is about 10 ns.[18] If one makes a reasonable assumption that the infinite frequency dielectric constant (ε_∞) of water in the water pool of the microemulsions is same as that of ordinary water, *i.e.* 5, then the solvent relaxation time, $\tau_s = (\varepsilon_0/\varepsilon_\infty)\tau_D$, should be about 1.67 ns which is close to the observed solvation time

in the AOT microemulsions.

Nanosecond solvation dynamics due to ions in solutions as well as molten salts, is well documented in the literature.[25] Thus one can not rule out the possibility that the observed nanosecond dynamics in the water pool is due to solvation by the Na$^+$ counter ions present in the water pool for the AOT microemulsions. To settle this issue, Mandal *et al.* 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.[26] The triton X-100 microemulsion also exhibits nanosecond solvation dynamics. This suggests that the ionic solvation dynamics plays 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 (C-343) in lecithin and AOT microemulsions using femtosecond upconversion.[27-29] For lecthin microemulsions, the solvent relaxation displays a very long component which does not become complete within 477 ps.[27] This is similar to the nanosecond dynamics reported earlier.[22-23] For Na-AOT, the solvation dynamics reported by Levinger *et al.* for the charged probe C-343 is faster than that reported by Bright *et al.* and Sarkar *et al.* The C-343 anion is expected to reside far from the AOT anion and hence, 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, acetonitrile and methanol in AOT microemulsions.[30-31] Using a picosecond setup, Shirota and Horie 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.[30]

c) *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 movement of the water molecules may be considerably constrained in the Stern layer. Solvation dynamics in micelles has been studied using C-480 and 4-AP as probes.[32-35] 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. It is observed that for SDS, CTAB, and TX-100, the average solvation times are respectively 180 ps, 470 ps and 1450 ps for C-480 and 80, 270 and 720 ps for 4-AP.[32-33] The solva-

tion 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.[12] 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[19]), about 10 times faster than that in the water pool of the microemulsions,[22-23] and is slightly faster than the longest component of solvation dynamics in γ-CD.[19] 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.[34] and hence, is too slow to account for the subnanosecond 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.

d) *Lipids*: Lipid vesicle refers to an aqueous volume enclosed by a bilayer of surfactants and dispersed in water. The interesting issue of the dynamics of the water molecules inside the water pool of the vesicles has been addressed very recently. Datta *et al.* studied C-480 in sonicated unilamellar DMPC vesicles.[35] The position of emission maximum of C-480 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.* 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%).[35] This result is very similar to the solvation dynamics of the same probe in the large water pools of AOT microemulsions.[22] The chain dynamics of DMPC occurs in the 100 ns time scale.[34]. Thus the nanosecond solvation dynamics in lipids is not due to the chain dynamics. Since in the bulk water the solvation dynamics is much faster (0.31 ps[19]) the results reported by Datta *et al.* demonstrates restricted motion of the water molecules in the inner water pool of the vesicles.[35]

e) *Sol-gel Glass and Polymer Hydrogels*: Due to the very high bulk viscosity of the semirigid hydrogels, and sol-gel glass one expects very slow relaxation of the water molecules in these media. Surprisingly very fast solvation and rotational relaxation dynamics have recently been reported in sol-gel glass[36] and in polyacrylamide (PAA) hydrogel.[37] The fast dynamics in the sol-gel glass and hydrogels have been attributed to the porous structure of these media. In the case of PAA the pores are large enough for big bio-molecules (*e.g.* DNA) to pass through during gel-electrophoresis. Thus the motion of the small water molecules or solvation dynamics is essentially free in these media. This is consistent with the very low microviscosity of these media reported by Tamai

et al.[38] and Claudia-Marchi *et al.*[39] and the large diffusion coefficients in these media.[40]

Proton Transfer Processes in Organized Assemblies

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.[41] As a result, the proton transfer processes in the organized assemblies differ considerably from those in the ordinary solutions. We have studied excited state proton transfer (ESPT) of two probes in various organized assemblies. ESPT is the main nonradiative pathway in the excited state of many biological probes, such as the popular DNA probe ethidium bromide (EB).[46] On addition of DNA, EB readily intercalates in the double helix of DNA in aqueous solutions. The intercalation causes nearly 11 fold increase in the emission intensity and lifetime of EB.[46-47] It is proposed that water quenches emission of EB by abstraction of the amino proton of the ethidium ion.[46] Since on intercalation in the DNA double-helix the ethidium ion becomes inaccessible to bulk water the quenching process is prevented and this leads to the fluorescence enhancement. 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.[48] Polarity of acetone (dielectric constant, ϵ=20.7 and $E_T(30)$=42) is less than that of another polar, aprotic solvent, acetonitrile (ϵ=37.5 and $E_T(30)$=46). 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.* 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.[49] 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.

In AOT microemulsions, presence of the negatively charged head group causes a sharp gradient in pH/pOH over the nanometer sized water pool. Menger and Saito reported that the acid-base property of *p*-nitrophenol (PNP) gets substantially modified in AOT microemulsions.[50] While in bulk water, at pH=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 pH 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.[50] 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. 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 properties is similar to that in bulk water.[51] Okazaki and Toriyama studied the location of an organic acid at different pH in AOT microemulsion, using ESR spectroscopy.[52] They observed that at low pH, when the molecule is in the neutral form, it stays close to the AOT-water interface, while at high pH the carboxylate anion is expelled from the AOT-water interface to the water pool.

The sharp local variation of pH in the water pool of the AOT microemulsions affects the intermolecular proton transfer process quite strongly. In ordinary aqueous solutions emission of ethidium bromide (EB), is strongly quenched by the hydroxyl ions. However, in AOT microemulsion, the hydroxyl ion does not quench the emission of EB, at all even when a highly alkaline aqueous solution of EB (pH=12.6) is injected into the reverse micelle.[49] 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.

In aqueous solutions 1-naphthol undergoes very fast deprotonation in the excited state in 35 ps time scale.[41-44] Fleming *et al.* reported that the rate of deprotonation of 1-naphthol is retarded 20 times inside cyclodextrin cavities.[43] Mandal et al. reported dramatic reduction in the rate of excited state deprotonation of 1-naphthol, from 35 ps in bulk water to the nanosecond time scale in micelles.[45] The marked retardation of the proton transfer process of 1-naphthol results in 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, 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.[42] 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.[45] The dramatic reduction in the rate of deprotonation of 1-naphthol in micelles is attributed to the non-availability of adequate number of protons to solvate the proton in the micellar environment.

Surface Second Harmonic Generation

In recent years surface second harmonic generation (SSHG) and sum frequency generation (SSFG) have been demonstrated to be two extremely powerful techniques to study selectively

a wide variety of surfaces.[53-54] In the present article we will restrict ourselves to only the air-water surface. In a SSHG experiment one measures three properties of the SSH light, namely, intensity, polarization and phase. They are related respectively to the number, relative orientation and absolute orientation of the surface species. The quantum chemical expression of the second order nonlinear susceptibility, which is related to the intensity of the SSH light, contains energy denominator of the form (ΔE-hν) and (ΔE-2hν). When the energy of one (hν) or two (2hν) laser photons becomes equal to the energy gap (ΔE) of the surface species the SSH signal intensity becomes very high. This situation is referred to as one- and two-photon resonance. The SSH signal of a resonant species is very high compared to that of a non-resonant species. Thus if more than one species are present at the surface using resonance SSHG one can study specifically one surface species. We have utilized this principle to find out how several non-resonant (*e.g.* urea, salts and a surfactant CTAB) affects the population of a resonant species *p*-nitrophenol (PNP) at the water surface. It is observed that salting-in agents like urea and salts containing big ions decrease population of PNP at the water surface.[55] It may be recalled that these agents are known to increase solubility of organic molecules in bulk water by modifying water-organic interactions.[3] Due to the very strong water-water attractions and the relatively low water-organic attractions organic molecules tend to avoid water.[3] This leads to low solubility of organic compounds in water, hydrophobic binding and also enrichment of water surface by organic molecules.[3] The increased interaction between water and organic molecules in the presence of the salting-in agents pulls the PNP molecules from surface to bulk causing a decrease in the surface population. Salting-out agents, *e.g.* salts having small ions weakens water-organic interaction and as a result the push the PNP molecules from bulk to surface causing an increase in surface population.[56] The surfactant CTAB is found to increase the surface population of PNP. The long alkyl chains of the CTAB molecules float on water surface. Thus in the presence of CTAB the air-water surface resemble at least partially an oil-water surface. Since PNP is more soluble in an oil than in water, it enriches the surface. This is very similar to enrichment of bio-membranes by small organic molecules.[55]

CONCLUSION

The recent studies on organized assemblies using ultrafast lasers has significantly improved our understanding of the structure, dynamics and spectroscopy of molecules in confined environments. The ultimate goal of ultrafast spectroscopy is to unravel the dynamics in complex biological and supramolecular assemblies. The results outlined in the present article show how dramatically the dynamics of ultrafast processes in confined media differ from those in ordinary homogeneous fluid media. As an outcome of these studies the behaviour of confined or biological water is now under-

stood almost quantitatively. Due to the inherent complexity of the organized molecular assemblies quantitative understanding of all the issues still elude us. Nevertheless, the recent progress in this area shows immense promise and since the general problem of dynamics in organized assemblies is still relatively unexplored one expects a very vigorous activity in this area in the near future.

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