FEATURE ARTICLE

Slow Dynamics of Constrained Water in Complex Geometries

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Although water is often hailed as the lubricant of life, a detailed understanding of its role in many chemical and biological processes still eludes us. In many natural systems, water is confined in an environment where its free movement is restricted and its three-dimensional hydrogen-bonded network is disrupted. Very recently, several groups applied ultrafast laser spectroscopy to study the dynamics of the constrained water molecules. It is observed that the dynamic behavior of the confined water molecules is markedly different from that of the ordinary water molecules. The most striking result is the bimodal response of confined water, with one bulk water-like subpicosecond component and a much slower component in a time scale of hundreds or thousands of picoseconds. This slow second component constitutes 10−30% of the total response and is crucial in the understanding of the role of water in complex chemical and biological processes. The origin of the slow component has been a subject of intense recent debate and has recently been attributed to a dynamic exchange between free and bound water. This interpretation seems to be in accord with the conclusion reached independently by intermolecular solute−water NOE and NMRD studies. In this article, a review of the recent experimental and theoretical work in this area is presented.

1. Introduction

The ubiquitous water molecule plays a unique role in controlling structure, dynamics and reactivity in natural systems.[1] The water molecules present in natural and biological systems are loosely described as natural or biological water. However, as pointed out by Kuntz and Kauzmann[1d] long ago, it is difficult to provide even an operational definition of the water of hydration of the biological systems. *Natural* water is never pure and is quite different from the pure water studied experimentally or simulated in a computer. Recent experimental results suggest that the difference between the two is so great that pure water, in many cases, ceases to be a guide in the understanding of the natural water. In natural systems, the water molecules often remain confined in self-organized molecular assemblies. The self-organized assemblies are molecular aggregates which are formed spontaneously in nature and are held together by weak intermolecular attractions.[1−5] Examples of water molecules in such restricted environments are abundant in nature and within the human body. One may cite, for instance, water in plants, fruits or blood vessels, in foam, in micelles or water pool of reverse micelles, on the surface and interior of proteins and in the grooves of DNA, in porous rocks, and so on.

The anomalous properties of pure water are usually ascribed to its extended hydrogen-bonded network. Dynamics of pure water has been studied quite extensively by solvation dynamics or dielectric relaxation.[6−11] Pure water exhibits fast dielectric relaxation[11] and very fast solvation dynamics[8,9] which occur, respectively, in a few picosecond and subpicosecond time scale. The very fast dynamics of water has been attributed to the intermolecular hydrogen-bonded structure and the resulting low-frequency intermolecular vibrational modes.[9−12] MD simulations suggest that in pure water the very fast motion of a water molecule is cooperative and involves coupling of different degrees of freedom.[12] Recently, several groups studied dynamics of the water molecules confined in various self-organized assemblies.[13−21] The hydration layer of the organized assemblies is heterogeneous in molecular length scale. As discussed by Halle,[18a] different experimental and theoretical methods probe such systems on different scales of time, length and energy. Consequently, the results of different studies sometimes appear to be conflicting. Fortunately, in recent years the situation has improved considerably and some general consensus has started to emerge. The most interesting discovery made so far is the bimodal nature of the dynamics of water in such restricted environments. The bimodal response of confined water consists of one subpicosecond component and a second, very slow component in the hundreds to thousands of picoseconds range. The first component is similar to that in bulk water. The very slow second component, on the other hand, is completely absent in pure water. The origin of this slow component is a subject of intense ongoing debate.

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At present, numerous techniques are available for studying the dynamics of liquids. Among them, the time-dependent fluorescence Stokes shift (TDFSS) and the more recent three photon echo peak shift (3PEPS) techniques stand out for their superior time resolution down to the femtosecond time scale.[6,7] The slow component of relaxation of the confined water molecules has recently been detected in neutron scattering,[1c] dielectric relaxation,[16,17] nuclear magnetic relaxation dispersion (NMRD)[18] and intermolecular water-solute nuclear Overhauser effect (NOE) studies.[19] Among the NMR techniques, the NMRD technique[18] provides the best time resolution while the intermolecular NOE offers excellent spatial resolution.[19] According to NMR studies, the residence time of protein bound water molecules ranges from picoseconds to milliseconds.[18,19] The combined picture which emerges from all these techniques, namely, neutron scattering, NMR, ultrafast laser spectroscopy and dielectric relaxation, is that the water molecule confined in the nanospace within an organized assembly is fundamentally different from water in the bulk. In the present article, we will review mainly the recent TDFSS and to a small extent, 3PEPS studies of dynamics of water molecules in several restricted environments.

The plan of the review is as follows. In section 2, we will briefly discuss the basic principles of the solvation dynamics studies. In section 3, we will discuss the recent experimental results and available theoretical explanations on a variety of organized assemblies. In section 4, we will try to develop a unified picture of the mechanism of slow relaxation and discuss different plausible theoretical models. Finally, in the concluding section we will present a future perspective.

2. Solvation Dynamics: General Features

Solvation refers to the stabilization of a solute molecule because of its interaction with the surrounding solvent molecules. Evidently, solvation is most pronounced when the solute is ionic or dipolar and the solvent is polar. The dynamics of this process, i.e., how quickly the solvent dipoles rearrange around an instantaneously created charge (electron) or dipole, is known as solvation dynamics. There are many molecules whose dipole moment is zero or very small in the ground electronic state while it is very large in the electronically excited state. Such a molecule exhibits a very prominent red shift of the absorption and the emission maximum with an increase in solvent polarity.[22] When such a solute molecule in a solution is excited by an ultrashort light pulse, a dipole is created instantaneously. Initially, the solvent dipoles remain randomly oriented around the solute dipole. Since the dipolar solute is in the excited state, it emits continuously. With an increase in time, the solvent dipoles gradually reorient and the energy of the excited dipole decreases. Thus, with an increase in time the emission maximum shifts to lower energy, i.e., toward longer wavelength. This phenomenon is known as time dependent fluorescence Stokes shift (TDFSS).[6−9] The molecular structures of a few probes, commonly used to study solvation dynamics using TDFSS, are given in Figure 1. The solvation dynamics is monitored by the decay of solvation time correlation function $C(t)$ which is defined as

$$C(t) = \frac{E(t) - E(\infty)}{E(0) - E(\infty)} \tag{1}$$

where $E(0)$, $E(t)$ and $E(\infty)$ denote the observed emission energies (frequencies) at time zero, t and infinity, respectively. If the decay of $C(t)$ is single exponential, e.g., $C(t) = \exp(-t/\tau_s)$, the time constant (τ_s) of the decay is defined as the solvation time. If the decay of $C(t)$ is multiexponential, i.e., $C(t) = \Sigma a_i \exp(-t/\tau_i)$, one uses the average solvation time $\langle\tau_s\rangle = \Sigma a_i\tau_i$. According to the continuum theory, the solvation time, τ_s, is given by

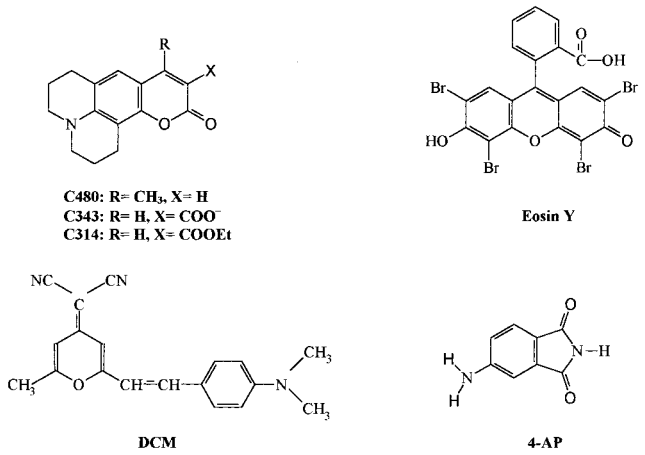

Figure 1. Structure of some common probes used to study solvation dynamics: coumarin dyes (C480, C343, C314), eosin Y, DCM (4-(dicyanomethylene)-2-methyl-[6-*p*-(dimethylamino)styryl]-4*H*-pyran), and 4-aminophthalimide (4-AP).

$$\tau_s = \frac{2\epsilon_\infty + \epsilon_C}{2\epsilon_0 + \epsilon_C} \tag{2}$$

where ϵ_∞ and ϵ_0, are respectively the high frequency and static dielectric constant of the solvent and τ_D is its dielectric relaxation time.[6,7] ϵ_C is the dielectric constant of the cavity surrounding the probe. For water, τ_D is 8.3 ps, while ϵ_∞ and ϵ_0, are respectively about 4.86 and 78.5.[6,7,11] Thus, according to the continuum theory, the solvation time of pure water is about 0.5 ps. Actual experimental results are close to this. In the first study of solvation dynamics in water, Barbara et al. reported that the solvation dynamics is biexponential with two components of 0.16 ps (33%) and 1.2 ps (67%) for coumarin 343 (C343).[8a] Later using better time resolution, Fleming et al. detected a Gaussian component of frequency 38.5 ps^{-1} and a biexponential decay with time constants 126 and 880 fs, respectively.[9] Subsequent studies on solvation dynamics with many dye molecules indicate that the dynamics of solvation in water is indeed ultrafast and occurs in the femtosecond scale.[6−11] As noted earlier, the ultrafast components of solvation dynamics in water has been explained in terms of the intermolecular vibration and libration modes of water.[9−10,12]

All organized media are essentially heterogeneous. For example, in an aqueous solution of a protein while bulk water is highly polar and exhibits fast dynamics, in the interior of the proteins, polarity is much less and the dynamic response is markedly different. Solvation dynamics largely probes the local dynamic properties of the water molecules around the solute molecule. This may give rise to two different situations. First, the probe molecule may remain immobilized at a certain location (e.g., by covalent attachment). Even in such a case, different probe molecules may experience different local properties at different sites. In the other scenario, due to molecular diffusion, the probe molecule may undergo excursion over a distance within its excited-state lifetime. As a result, the probe reports the average property of a region, a few nanometers in radius. Note that this complication, arising from the inherent uncertainty in the position of the fluorophore, is absent in a homogeneous

liquid. Since the dimension of the confined region in an organized medium is on the order of a few nanometers, it is essential to ensure that the fluorescent probe is located within the microenvironment under study. Fortunately, the spectroscopic properties (absorption/emission maximum, and fluorescence lifetime) often serve as good indicators to ascertain the position of the probe. Also, the diffusion coefficient in a restricted environment is much smaller than that in a homogeneous liquid. Therefore, the region of excursion is small in a restricted medium.

It should be pointed out that dielectric relaxation or NMR techniques (except intermolecular NOE) offer no spatial resolution and, hence, do not report the local property within a confined environment. Many groups have used rotational relaxation to study various organized media.[23] A major complicating feature of the rotational relaxation studies in organized assemblies is that the overall motion of the macromolecules is superimposed on the rotational dynamics of the probe solute. Consequently, the rotational dynamics of a small probe in an organized medium, is dominated by the overall tumbling and collective bending and twisting motions of the macromolecules.[23] On the other hand, solvation dynamics directly probes the response of the small solvent molecules confined in the immediate vicinity of the probe solute. Since solvation dynamics is very fast it is rather insensitive to the much slower motion of the macromolecular chains. Even the slow component of solvation dynamics discussed here occurs at a time scale which is at least 1 order of magnitude faster than the motion of either of the probe or the substrate. Thus, solvation dynamics is a simple, direct and sensitive tool to investigate the local dynamics in a restricted environment. In the following sections, we will show that though in many cases, results of the solvation dynamics studies are very similar to those of dielectric relaxation and NMR studies, in some cases they differ. This may presumably arise from of the water molecules in different regions of the organized assemblies, probed by different techniques. In these complex systems containing a variety of polar entities, it is difficult to separate unambiguously contributions of bound or constrained water in many cases. Nevertheless, we will see a large volume of experimental data may be interpreted in terms of motion of constrained water.

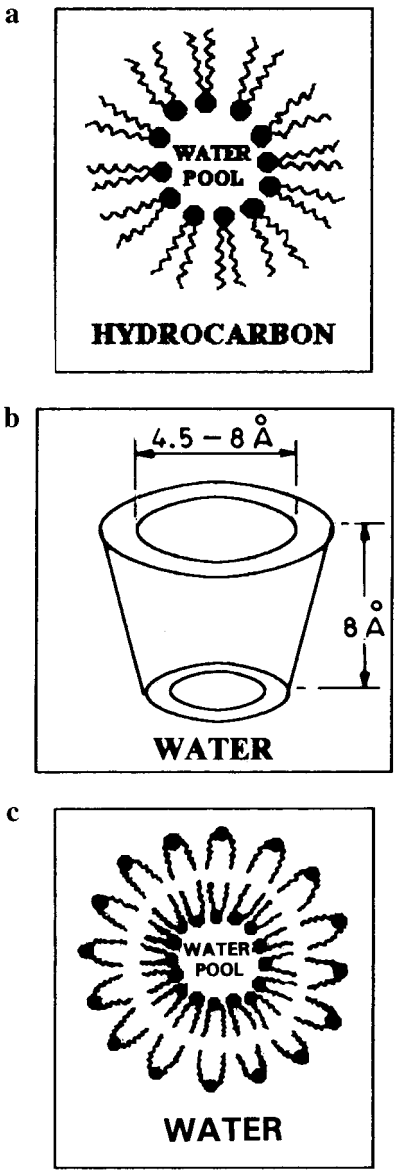

Figure 2. (a) Schematic diagram of a microemulsion. (b) Schematic diagram of a cyclodextrin. (c) Schematic diagram of a lipid.

3. Solvation Dynamics in Organized Media

To interpret the TDFSS results quantitatively, it is essential to have the knowledge of the structure and dielectric relaxation times of the organized assemblies. Fortunately, this information has recently become available.[24] Structures of a few organized assemblies are depicted in Figure 2. In this section, we will discuss the dynamics of water (and in a few cases of other liquids) in various confined environments. We will also try to develop at least a semiquantitative picture of the solvation dynamics in these complex systems.

3.1. Reverse Micelles and Microemulsions. The reverse micelles or the microemulsions are elegant examples of confined water molecules. They refer to the aggregates of surfactants formed in a nonpolar solvent. In such an aggregate, the polar headgroups of the surfactants point inward and the hydrocarbon chains project outward into the nonpolar solvent.[25−28] A reverse micelle may encapsulate fairly large amounts of water in form of a nearly spherical droplet which is called a water pool. In the case of AOT (aerosol-OT, dioctyl sulfosuccinate, sodium salt) up to 50 water molecules per molecule of the surfactant can be trapped in this manner.[25−28] Such a hydrated reverse micelle (Figure 2a) is called a microemulsion. The radius (r_w) of the water pool is found to vary linearly with the water to surfactant mole ratio, w_0. For AOT, r_w is approximately equal to $2w_0$ (in Å) in *n*-heptane.[25c] The water molecules confined in the water pool of a microemulsion differ in a number of ways from bulk water. All the water molecules in a microemulsion, except the six most tightly held ones freeze at −50 °C.[25,26,28] Quist and Halle[26b] studied relaxation of unfrozen water in microemulsions at sub-zero temperature using water ^{2}H relaxation and found that the relaxation time is 2 orders of magnitude slower than that of D_2O at same temperatures. The recent compressibility measurements indicate that the first solvation shell of AOT becomes complete at $w_0 = 13$ and up to this point the water structure within the water pool remains severely perturbed.[26a] But even in large water pools ($w_0 > 13$), the compressibility of the microemulsion remains at least two times higher than that of ordinary water.[26a] Several groups have studied dielectric relaxation of confined water in microemulsions. D'Angelo et al.[27a] studied dielectric relaxation of AOT−water−carbon tetrachloride microemulsion in the 0.02−3 GHz frequency range as a function of the water to AOT molar ratio, $0.2 < w_0 < 10$. They detected a single relaxation time of about

7 ns at the lowest water content, which becomes faster with increase in w_0. D'Angelo et al. attributed this to micellar tumbling and motion of individual surfactants. On the other hand, Mittleman et al.[27b] studied the fast components of dielectric relaxation of microemulsions in the tera-hertz frequency range and observed that that the relaxation time is only slightly slower than that in bulk water. These two studies are complementary and should be considered together to identify the fast and slow dynamics.

Solvation dynamics in the confined water pool of microemulsions has been the subject of many recent studies.[29−32] In a heterogeneous microemulsion system, the probe may reside in any of the following three regions- in bulk nonpolar solvent, in the water pool or between the surfactants. In the case of an ionic probe (e.g., C343, Figure 1)[32] one may rule out the possibility of the probe staying in bulk nonpolar medium or among the hydrocarbon chains of the surfactant. In this case, one may safely assume that the probe stays in the water pool exclusively. For neutral probes, like C480,[30a] 4-AP,[30b] or DCM[30c] (see Figure 1) some of the probe molecules may stay in the bulk nonpolar solvent. However, since these probes do not exhibit solvation dynamics in the bulk nonpolar solvent one may neglect their contribution to the observed solvation dynamics.

Solvation dynamics in AOT/*n*-heptane/water microemulsion has been studied using various probes.[29−32] In a microemulsion, a distinct growth in the nanosecond time scale is observed at the red end of the emission spectrum.[30] This clearly indicates the existence of a slow nanosecond component for the solvation dynamics in the water pool. Figure 3 displays the fluorescence decays, time-resolved emission spectra and decay of $C(t)$ for 4-AP in AOT.[30b] Sarkar et al. observed that in a small water pool ($w_0 = 4$), the solvation time is 8 ns while for a very large water pool ($w_0 = 32$) the response is bimodal with a fast component of 1.7 ns and a slower component of 12 ns.[30a] The appearance of the nearly 1.7 ns component in the large water pools indicates that even in the large water pools of the microemulsions, the water molecules are about 5000 times slower than that in the bulk water. In a big water pool ($w_0 > 10$), it is observed that the solvation time is 1.9 ns for 4-AP[30b] and 1.2 ns for DCM.[30c] This indicates that the solvation dynamics in big water pools is reasonably independent of the probe. Several groups have studied solvation dynamics in reverse micelles using phase fluorimetry.[31] Bright et al. studied the solvation dynamics of acrylodan-labeled human serum albumin in AOT microemulsion and observed that the solvation time is 8 ns in a small water pool and 2 ns in a large water pool.[31a]

A semiquantitative explanation of the nanosecond component, may be as follows. The static polarity or the dielectric constant of the water pool of the AOT microemulsions may be estimated from the position of the emission maximum of the probes.[30] For all the probes, the water pool resembles an alcohol like environment with an effective dielectric constant in the range 30−40. It is reasonable to assume that ϵ_∞ of water in the water pool of the microemulsions is same as that in ordinary water.[6,7] Then using the experimentally determined dielectric relaxation time of the microemulsion of about 10 ns,[27a] the solvent relaxation time is calculated to be $(5/30) \times 10 \approx 1.67$ ns. This is indeed close to the observed solvation time in AOT microemulsions. However, there are two problems with the above analysis. First, it is not clear why the dielectric constant of the water pool is so low. Second, the origin of the slow dielectric relaxation is also not clear. Both these two issues will be addressed below.

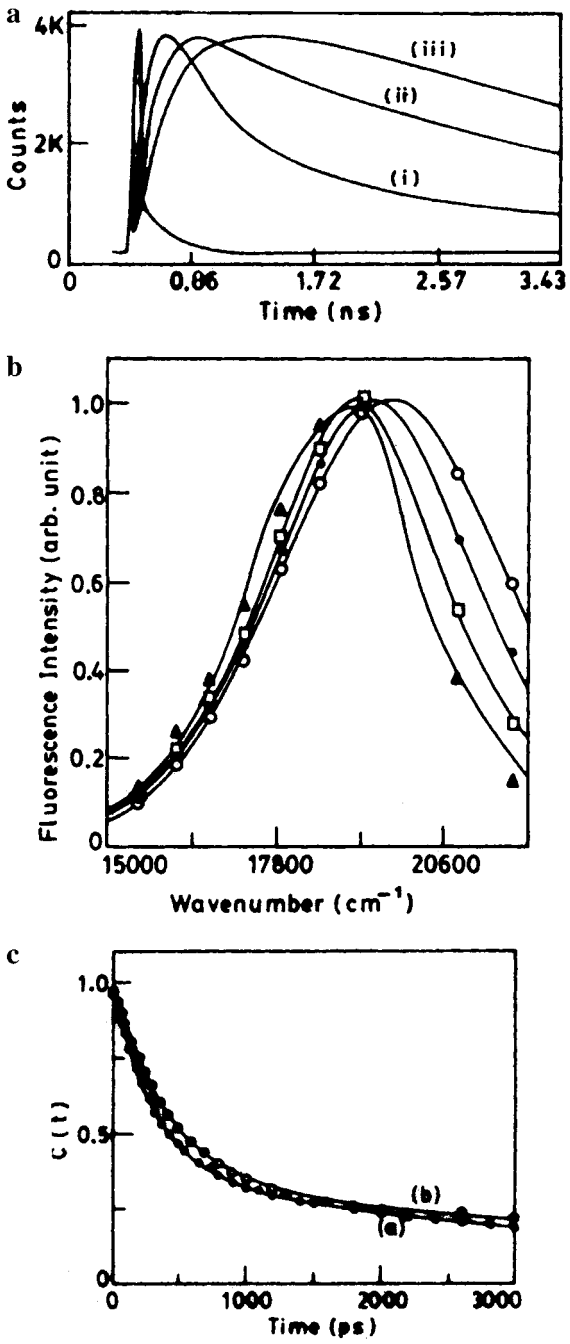

Figure 3. (a) Fluorescence decays of 4-AP in the water pool of AOT microemulsions, $w_0 = 12$ at (i) 460 nm, (ii) 500 nm, and (iii) 645 nm.[30b] (b) Time-resolved emission spectra for 4-AP in AOT microemulsions at 0 ps (○), 150 ps (●), 425 ps (□), and 1600 ps (▲).[30b] (c) Decay of $C(t)$ for 4-AP in AOT microemulsions for H_2O (●) and for D_2O (○).[30b]

Of course one might (and one should) argue that the nanosecond dynamics observed in the water pool is not due to the slower water molecules but is because of the solvation of the probe by the Na^+-counterions present in the water pool for the AOT microemulsions. To examine this possibility, Mandal et al. studied solvation dynamics of 4-AP in a microemulsion containing neutral surfactant, triton X-100 where no ions are present in the water pool.[30d] The triton X-100 microemulsion exhibits nanosecond solvation dynamics with a major (65%) component of 0.74 ns and another very long component. This shows that the ionic solvation dynamics has little or no role in the solvation dynamics observed in the water pool.

For 4-AP, in a large water pool, the solvation time increases from 1.9 ns in H_2O to 2.3 ns in D_2O, displaying a 20%

deuterium isotope effect.[30b] Such a deuterium isotope effect on solvation dynamics in restricted environments is consistent with similar isotope effects on solvation dynamics and electron-transfer processes observed in homogeneous solutions.[33] The latter may be explained by the molecular hydrodynamic theory.[11] The exact cause of the isotope effect is somewhat less clear in the present case of microemulsions.

Levinger et al. studied the solvation dynamics of C343 (Figure 1) in lecithin and AOT microemulsions using femtosecond upconversion.[32] For lecithin microemulsions, they observed that the solvent relaxation is very slow and does not become complete within 477 ps.[32a] This is consistent with the nanosecond dynamics in microemulsion reported earlier.[30,31] For Na-AOT, Levinger et al.[32c] reported that the solvation dynamics of the charged probe C343 displays a slow component in the 200−400 ps time scale. This component becomes faster with increase in w_0. But even at $w_0 = 40$, the solvation dynamics is found to be slower than that in water.[32c] NMR studies, however, suggest that at room temperature, the relaxation time of water in microemulsions is only about an order of magnitude slower than that of bulk water.[26c]

Apart from water, many other polar solvents may be trapped in microemulsions. Very recently, several groups studied solvation dynamics of nonaqueous solvents in AOT microemulsions.[34] Levinger et al. reported that in a microemulsion containing formamide the solvation dynamics exhibits a component of 240 ps which is nearly 250 times slower than that in bulk formamide.[34a] Shirota and Horie[34b] found that in AOT microemulsion, the solvation dynamics of acetonitrile and methanol is nonexponential and each is about 1000 times slower than that in the corresponding bulk solvents. They attributed the nonexponential decay to the inherent inhomogeneous nature of the solvent pools. Castner et al.[35] earlier developed an "inhomogeneous dielectric continuum model" using a position dependent dielectric constant, $\epsilon_0(r)$. Although this model appears to be quite appropriate for microemulsions, it is rather difficult to apply because of the lack of knowledge of a proper form of $\epsilon_0(r)$.

One should note that in the slower picosecond setup used by Bhattacharyya et al.[30] or Shirota and Horie[34b] a substantial portion of the solvation dynamics which occurs in femtosecond time scale might have been missed. Fee and Maroncelli[7c] developed a method to estimate the emission energy at $t = 0$. Using this, one can calculate the amount of solvation missed in a picosecond setup. If the probe is excited at its absorption maximum (ν_{abs}), the emission energy at time-zero, $\nu_{em}(t=0)$ is given by a rather simple relation,[7c]

$$\nu_{em}(t=0) \approx \nu_{abs} - [\nu_{abs}(\text{nonpolar}) - \nu_{em}(\text{nonpolar})] \quad (3)$$

where, ν_{abs}(nonpolar) and ν_{em}(nonpolar), respectively, denote the absorption and emission frequencies of the same probe in a reference nonpolar solvent. If the wavelength of excitation for time-resolved studies is different from the absorption maximum (ν_{abs}), the procedure of calculation of $\nu_{em}(t=0)$ is a bit cumbersome.[7c] In many organized assemblies, it is observed that a substantial portion of the solvation occurs in <100 fs time scale.[39,53−54] It is clear that the amplitude of the slow component will vary from system to system. For example, this amplitude can be very high for reverse micelles with low w_0 but may become small for large w_0. In summary, it appears certain that in many organized assemblies solvation dynamics of water (and other liquids) exhibits a component markedly slower than those of the same liquids in bulk.

Several theoretical studies have attempted to explain the dramatically slow component of solvation dynamics in microemulsions. The dynamics of water in microemulsions has been investigated using computer simulation.[36] Brown and Clarke carried out a MD simulation using a simplified single-site interaction model.[36a] Linse performed a simulation in which the interaction of the hydrophobic cavity, water molecules, and the counterions was represented by a simple potential, the spherical equivalent of the 9-3 potential while the water−water, water−sodium ion and sodium−sodium potentials are based on ab initio quantum chemical calculations.[36b] Though this model does not correspond exactly to a microemulsion, results of this simulation indicate a 2−4 times slowing down of motion of water in the pool compared to that in bulk water.[36b] In an interesting MD simulation, Senapathy and Chandra[36c] modeled the water pool of a microemulsion as a Stockmeyer liquid confined in a smooth spherical cavity. They used a 9-3 Lennard-Jones potential to describe the interaction of the confined water with the surrounding cavity wall. This model is rather oversimplified as it ignores the presence of any ions (both the ionic surfactants and counterions). However, this study[36c] helps in separating the finite size effect from other chemical effects such as hydrogen bonding of the water molecules with the surfactant. Senapathy and Chandra[36c] found that the dielectric constant increases as the cavity size (size of water pool) increases. They also found a nearly 5 times slowing down of solvation dynamics on confinement.[36c] Thus, the simulation of Senapathy and Chandra[36c] reproduces qualitatively some of the features of solvation dynamics in microemulsion. Recently, Faeder and Ladayni[36d] used a model very similar to that of Linse[36b] with a more realistic representation of the AOT and taking into account many experimental quantities explicitly. In this model, the surfactants were considered to be a pair of atomic ions and the interaction potential as a sum of point charge and Lennard-Jonnes terms. They used the SPC/E model of water for both charge distribution and Lennard-Jonnes interaction.[36d] The main limitation of this study[36d] is that it did not include the relaxation of the surfactant molecules which were held rigidly fixed. The simulation carried out by Faeder and Ladayni[36d] clearly shows that at small w_0 (=1) nearly all the counterions remain bound to the surfactant. With rise in w_0, solvent separated ion pairs are formed and an increasing amount of the counterions become detached from the surfactant. By $w_0 = 10$, the surface lattice (formed by surfactants, counterions and trapped water molecules) was found to be completely destroyed and density of water at the interface exceeds that in bulk. They[36d] identified three types of water molecules namely, the trapped, bound and free, proposed earlier to explain the IR spectra of microemulsions.[28] The translational and rotational mobility of the trapped and bound water were found to be slower than that of free water. Surprisingly, the preliminary results reported by Faeder and Ladayni, do not indicate slowing down of the solvation dynamics in the water pool.[36d] This is apparently in conflict with the experimental results.[29−32] It is possible that Faeder and Ladanyi[36d] missed the slow relaxation component in nanosecond time scale, as the simulation was not long enough to detect the interconversion between the free and the bound water molecules. Senapathy and Chandra[36c] did not have this limitation, as they simulated a simple Stockmeyer liquid confined in a smooth structure-less cavity.

A multishell continuum model has recently been used to explain the slow solvation dynamics in the water pool of the reverse micelles.[37] This theory predicts that at low water content the solvation time correlation function decays at a rate slower

than that in the bulk water. As the water content (that is, w_0) is increased, the decay of the solvation time correlation function becomes faster. However, even at very large w_0, solvation dynamics remains much slower than that in bulk water.[37] These results are in good agreement with the experimental results.[30,31] Although the initial theoretical models are quite promising, it is evident that a complete understanding of the dramatically slow component needs further improvement of the models. Theoretically, the problem is highly nontrivial because the polar surface of the micelle strongly perturbs the extended hydrogen bond network of water. Strong hydrogen bonding with the micelle introduces two kinds of competing correlations which results in a frustration of the hydrogen bond network.

3.2. Cyclodextrin. Cyclodextrins (CD) are cyclic polymers of the sugar, α-amylose.[38] CD-s having 6, 7, and 8 amylose units are called α, β and γ-CD, respectively, and their diameters are 4.5, 6.5, and 8 Å, respectively.[38] CD-s are highly soluble in water and encapsulate organic molecules of suitable size. Structure of CD-inclusion complexes have been studied by crystallography[38a] and simulation.[38b]

Vajda et al. first studied solvation dynamics of C480 and C460 in a γ-CD cavity, using time dependent fluorescence Stokes shift (TDFSS).[39] Addition of γ-CD to an aqueous solution results in a marked blue shift in emission maximum and increase in fluorescence lifetime, for both the dyes.[40] This indicates that the dye molecules remain encapsulated in the γ-CD cavity. Vajda et al. found that the initial component of solvation in γ-CD is similar to that in bulk water.[39] However, it is observed that at longer times, the solvent response in γ-CD is significantly slower and is described by three components of 13, 109, and 1200 ps for C480.[39] Recently a theoretical study of the solvation dynamics in cyclodextrin has been carried out using a multishell continuum model (MSCM) and molecular hydrodynamic theory (MHT).[41] The latter theory suggests that the slow decay at long time, may arise because of the freezing of the solvent translational modes within the γ-CD cavity. Note that the freezing of the translational modes should seriously affect the orientational motion. This nonlinear effect has not yet been studied in detail. Comparison of the results of the MSCM and MHT calculations shows that while the molecular approach certainly gives a better agreement with experiment, a continuum theory in which the dielectric behavior of the different solvent zones is properly included could also give satisfactory results.[41]

3.3. Micelles. In water or a few other highly polar solvents, many surfactants form nearly spherical aggregates when their concentration exceeds certain critical concentration, called critical micellar concentration (cmc). These spherical aggregates are known as micelles. Recent small-angle X-ray[42a] and neutron scattering studies,[42b−d] indicate that the central region or core of a micelle is essentially "dry" and contains only the hydrocarbon chains. The core is surrounded by the Stern layer which consists of the ionic headgroups, bound counterions and water molecules. In a nonionic (e.g., polyoxyethylated) surfactant, the hydrocarbon core is surrounded by a palisade layer, which consists of the polyoxyethylene groups hydrogen bonded to the water molecules. Telgmann and Kaatze[43a,b] 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. They ascribed the fastest relaxation time to the rotation of the alkyl chains of the surfactants in the core of the micelle and the longest relaxation time to the exchange of monomer between bulk and the micelles. They did not assign the intermediate relaxation time to any particular motion. As we will see shortly, the nanosecond relaxation time may correspond to the solvent relaxation in the Stern layer.

In the case of the micelles, the possible locations of the probe are bulk water, the "dry" micellar core and the Stern layer. If the probe resides in the bulk water, obviously the slow part of the solvation will be in a few picosecond time scale. Since the core of the micelle resembles aliphatic hydrocarbons, the probe is not expected to exhibit dynamic Stokes shift in the core. However, if the probe stays in the Stern layer, its solvation dynamics may be quite different from that in bulk water. Solvation dynamics in neutral (triton X-100, TX), cationic (cetyl trimethylammonium bromide, CTAB) and anionic (sodium dodecyl sulfate, SDS) micelles have been studied using C480 and 4-AP as probes.[44a,b] Emission properties of the probes in the micelles are very different from those in water and in hydrocarbon. This indicates that the probes reside neither in bulk water nor in the core of the micelles and therefore, are certainly located in the peripheral Stern layer of the micelles. The average solvation times for anionic SDS, cationic CTAB, and neutral TX are respectively 180, 470, and 1450 ps for C480[44a] and 80, 270, and 720 ps for 4-AP.[44b] The solvation times in the micelles differ at most 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 readily seen that the solvation dynamics in the Stern layer of the micelles is 3 orders of magnitude slower than that in bulk water and is only slightly faster than the longest component of solvation dynamics in γ-CD.[39]

The main candidates causing solvation in the Stern layer of the micelles are the polar or ionic headgroups of the surfactants, the counterions (for SDS and CTAB) and the water molecules. According to ESR studies, the dynamics of the long alkyl chains of the surfactants occurs in the 100 ns time scale.[45a,b] Thus, the subnanosecond solvation dynamics in the micelles is not due to any motion of the alkyl chains. The rotational motion of the headgroups which occur in subnanosecond time scale,[43,45d] cannot account for the component of solvation in the nanosecond time scale. However, one cannot rule out totally its contribution to the fast component of solvation dynamics in the micelles. The role of ionic solvation by the counterions also appears to be unimportant because of the similar time scales of solvation for the ionic and the neutral micelles.

It is observed that for both the probes, the solvation time in TX is longer than that in CTAB and SDS. The difference in the solvation times in the three micelles may be explained in terms of the differences in their structure.[42] The hydrated shell for TX (25 Å) is thicker than that for SDS and CTAB (6−9 Å). Thus, for SDS and CTAB, a major portion of the probe in the Stern Layer sticks out into the bulk water. On the other hand, the palisade layer of TX is sufficiently thick to shield the probe completely from bulk water. This may be responsible for the slower solvation dynamics in the case of TX. It is readily seen that the solvation times in the micelles correspond rather nicely to the intermediate range of dielectric relaxation times (10 ns) reported by Telgmann and Kaatze.[43a,b] However, the water NMR relaxation studies by Carlstrom and Halle indicate that the dynamics of water in the micellar surfaces is only about 5 times slower compared to bulk water.[43c] The NMR results are in contrast with the results of the solvation dynamics and dielectric relaxation studies. We will discuss later the possible reason for the discrepancy between the results obtained using these three techniques. Detailed simulation or theoretical study of this highly interesting problem is not yet available.

3.4. Lipids. A lipid vesicle resembles most closely a biological cell.[45−50] A vesicle refers to an aqueous volume ("water pool") entirely enclosed by a membrane and dispersed in bulk water. The membrane is basically a bilayer of lipid molecules. In the case of unilamellar vesicles (radius ≈250 nm), 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 through sonication or by rapid injection of a concentrated ethanolic solution of the lipid to a buffered aqueous medium.[46] In such a system, there are two kinds of water molecules present,- bulk water 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). Recently, the structure of lipids, the dynamics of surfactant chains and transport through the membrane wall have been studied using spin probes,[45a,b] fluorescence of pyrene,[45c] computer simulation,[47] surface second harmonic generation[48] and dielectric relaxation.[49] The state of solvation of a fluorescent probe, in the unilamellar and multilamellar vesicles is often studied by red edge excitation spectroscopy (REES).[50] REES is based on the fact that in such an inhomogeneous medium the probe molecules in different regions remain in different states of solvation and as a result, exhibit different absorption and emission characteristics. This gives rise to the gradual shift in the emission maximum as the wavelength of excitation is changed. Evidently, REES arises as a result of the different extent of solvation of the probe molecules in the ground state and gives no information on the relaxation properties inside the vesicles. The extremely important issue of the dynamics of water molecules inside the water pool of unilamellar vesicle has been addressed recently.[51] Solvation dynamics in more than one lipids (dimyristoyl and dipalmitoyl phosphatidylcholine) has been studied using several probes.[51] It is observed that irrespective of the probe or the lipid, the solvation dynamics in lipid vesicles is biexponential with one component in the range 100−600 ps and another of 1−11 ns.[51] This result is very similar to the solvation dynamics of the same probes in the large water pools of AOT microemulsions.[30] As already discussed, the nanosecond solvation dynamics in lipids cannot be due to the chain dynamics of surfactants which occurs in the 100 ns time scale.[45] Since, the solvation dynamics in bulk water is much faster, the slow solvation dynamics clearly demonstrates the restricted motion of the water molecules in the inner water pool of the vesicles. The dielectric relaxation studies of lipid vesicles reveal two prominent components in 100 ps and 10 ns time scale.[49] The solvation dynamics studies[51] are thus consistent with the dielectric relaxation studies. NMR relaxation studies, however, suggest that the relaxation time of water in the primary hydration shell of phospholipid membranes is longer by less than a factor of 5 compared to bulk water.[47c]

3.5. Proteins and DNA. Among all the organized media, study of the water molecules in the immediate vicinity of a protein and a DNA molecule is most useful in understanding the behavior of biological water. Unfortunately, there are only a few studies on the dynamic properties of the protein environment. Pierce and Boxer[52a] and Bashkin et al.[52b] studied solvation dynamics in protein environments using dynamic Stokes shift and reported solvation times on the order of 10 ns and attributed this to protein dynamics. Most recently, Fleming et al.[53] and Beck et al.[54] employed respectively, three photon echo peak shift (3PEPS) and transient grating spectroscopy to study the dynamic properties of the protein environment. In all these studies, the probe is noncovalently bound to the protein and its exact location is uncertain.

It should be emphasized here that in the case of a protein, because of the presence of many charged side groups, even the definition of the dielectric constant is not straightforward. Recent simulations indicate that the static dielectric constant of a protein varies with position and depends quite strongly on what is taken into account explicitly in the model.[20] Because of these difficulties, Fleming et al. considered several dielectric continuum models to explain the solvation dynamics of eosin bound to lysozyme in aqueous solutions.[53] The 3PEPS technique used by Fleming et al. reveal the occurrence of dynamics over a range of time scale from subpicosecond to hundreds of picoseconds.[53] They reported an ultrafast component of 30 fs contributing to about 60% of the signal.[53] When they fitted the data to 1 ns, they detected a slow component of 530 ps with an amplitude of 8%.[53] The 530 ps component is not detected in the case of free eosin in bulk water.[9b] As a result, the 530 ps component is attributed to the water molecules near the protein. Appearance of such a long component demonstrates that the motion of the water molecules in the immediate vicinity of the protein is highly constrained.

The microenvironment of DNA is often studied using a probe which intercalates between its double helix.[55,56] Unfortunately, most probes which intercalate in DNA do not exhibit solvation dynamics. Very recently, Brauns et al. introduced solvation dynamics as a technique to study the microenvironment within DNA.[56a] For this purpose, they attached a probe C480 unit covalently to DNA.[56a] Such a covalently attached C480, probe the local dynamics within a specified region of DNA. It is observed that in DNA the covalently attached C480 exhibits a slow biexponential solvation dynamics with two components of decay of 300 ps (47%) and 13.4 ns (53%).[56a] This indicates significant retardation in the motion of water in the solvation shell of DNA. The time scale of the slow component corresponds to the δ-relaxation observed in dielectric relaxation of DNA which occurs in tens of nanoseconds.[56b] However, in their setup of time resolution of 100 ps, Brauns et al. missed a considerable part of solvation dynamics which occur in a time scale shorter than 100 ps. From the method of Fee and Maroncelli,[7c] the expected Stokes shift is about 1500 cm^{-1} for C480 covalently bound to DNA. Brauns et al., however, detected a Stokes shift of 312 cm^{-1}. This implies that they have missed nearly 80% of the solvation dynamics.[56a] While Brauns et al.[56a] ascribed the slow dynamics to DNA motions, Saif et al.[56b] attributed this to counterion motion. Halle et al. studied water dynamics in DNA using NMRD and found that the longest water residence time in the minor groove is about 200 ps.[57]

The slow solvation dynamics observed in aqueous solutions of the protein and DNA is consistent with the vast literature on the slow relaxation components detected in dielectric relaxation and NMR studies.[1,15−19] Several authors reported that aqueous solutions of many biological systems exhibit relaxation times with one component of 10 ps time scale (similar to bulk water) and another very slow component, which in some cases, is in 10 ns time scale.[15−17] NMRD studies indicate that the water molecules at the protein surface exhibit subnanosecond residence time while a few water molecules buried deep inside a protein display a long residence time (micro- to millisecond).[18] The NMRD method, as such, does not have spatial resolution. However, Halle et al. showed that one can assign the experimentally observed residence times to individual water molecules by comparing wild type and mutant variety of the same protein which differ in the number of buried water molecules.[18d] As

mentioned above, NOE offers spatial resolution down to intermolecular separation. The positive sign of the intermolecular NOE signal indicates that the vector connecting a protein proton with the proton of the neighboring hydration water molecule is modulated by a motion which is faster than the rotation of the protein.[19b] This motion may arise either from the exchange of water molecules in and out of the hydration layer of the protein or from a local reorientation of the water molecules in the layer.[19]

Recently, a general theoretical model has been proposed to explain the dielectric relaxation and other dielectric properties of water present in the immediate vicinity of a protein.[17] In this model, the water molecules present in the immediate vicinity of a protein are classified as free and bound water. The free water molecules retain complete orientational degrees of freedom and contribute to the dielectric relaxation process. The bound water molecules remain hydrogen bonded to the protein. As a result, their rotation is coupled with the rotation of the biomolecule and hence, they rotate slowly. In general, the water molecules attached to a macromolecule form fewer hydrogen bonds compared to a free water molecule in bulk water. The model assumes the following dynamic exchange between the free and bound water,[17]

$$(H_2O)_{free} \rightleftharpoons (H_2O)_{bound} \tag{4}$$

The energetics of the exchange depends on the strength and the number of hydrogen bond(s) of a bound water molecule with the biomolecule. As the strength of the hydrogen bond increases, both the relative population of the bound species and the exchange time increase. Consequently, the relative contribution and the relaxation time of the slow component also increase. An important aspect of this model is that the slow relaxation time comes from the free water molecules themselves as a consequence of the dynamic exchange embodied in eq 4.

Fischer et al.[21] carried out a reaction path calculation for the rotation of a water molecule buried in bovine pancreatic trypsin inhibitor. They found that the process is similar to the rotation of water molecules in ice and leads to the interchange of two water hydrogen atoms. The total pathway is found to be complex and involves two successive rotations about orthogonal axes.

3.6. Polymer Hydrogel, Sol−Gel Matrix and Nanoparticles. Several macroscopically solid materials trap a large amount of water. The most common examples are microporous polymer hydrogel[58−61] and sol−gel matrix.[62−64] The microporous synthetic polymer hydrogels refer to certain polymers which are inherently insoluble in water but can entrap considerable amount of water within their polymer networks.[58] On absorption of water such a hydrogel swells in size quite significantly. The pore size in such a gel can be easily varied by varying the concentration of the monomer. Among the various types of hydrogel, 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.

The bulk viscosity of most polymers and particularly the semirigid hydrogels is very high. Thus, at a first glance, one would expect a very slow relaxation of the water molecules in the polymer matrices and the polymer hydrogels. However, it is observed that in a polyacrylamide hydrogel, both solvation dynamics and rotational relaxation occur in <50 ps time scale.[60] This surprisingly fast solvation and rotational dynamics of small probe molecules in hydrogels have been attributed to the extensively porous structure of the hydrogels. In a hydrogel, these pores are so big that even large biomolecules pass through them quite easily and hence, the motion of the small water molecules or the probe molecules remain quite fast in a hydrogel. The surprisingly fast dynamics in a hydrogel is consistent with the recent studies on microviscosity and diffusion in these media. The NMR[61a] and simulation[61b] studies indicate that the diffusion coefficient of water molecules in polymer hydrogels is not appreciably slow compared to ordinary water and is smaller at most by a factor of 2 than that in ordinary water. Claudia-Marchi et al. found that for titania gels at the sol−gel transition point (when the bulk viscosity increases sharply), the emission anisotropy does not change perceptibly.[63] Thus, the microviscosity of the gel is low despite the high bulk viscosity. Similar high mobility in polyacrylamide hydrogel has been reported by Moerner et al.[59] Using fluorescence microscopy they demonstrated that almost all (98%) of the probe molecules (nile red) remain highly mobile in polyacrylamide hydrogel. Datta et al.[60] reported that 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 a lifetime of 1.3 ns. The other environment is quite aprotic in which 4-AP emits at 470 nm with a lifetime of 7.2 ns.[60]

The inorganic sol−gel composite obtained from the hydrolysis of tetra-alkyl ortho-silicate acts as a good host for many biological materials.[62] Many enzymes can be encapsulated in biologically active form for a very long period in a sol−gel glass. Sol−gel glasses doped with biomolecules have potential applications as chemical sensors. It is obviously interesting to find out the dynamics occurring in such an interesting material. However, there have been relatively few studies on relaxation dynamics in sol−gel matrices. Bright et al. studied relaxation of acrylodan labeled BSA in a sol−gel matrix using phase fluorimetry.[64] They reported that the protein molecule remains highly mobile in this matrix.[64] Fourkas and co-workers studied dynamics of methyl iodide and acetonitrile in sol−gel glasses of different pore sizes using optical Kerr effect (OKE).[65] They observed that for both the liquids the decay of the OKE signal in a sol−gel glass is multiexponential. The major component of the decay is similar to that in the bulk liquid. They found an additional component which is about 4 times slower. The ratio of the amplitudes of the fast (bulk) and the slow component increases with the pore size.[65] In their study, the size of the pores (>24 Å) is much bigger than the small probe molecules (methyl iodide and acetonitrile). Pal et al. recently studied solvation dynamics of water molecules trapped in tetraethyl orthosilicate (TEOS) sol−gel matrix using C480 as a probe.[66] The pore size of the sol−gel glass used by them is quite small (10−20 Å). It is found that in the rigid sol−gel matrix, the average solvation time is 220 ± 30 ps.[66] This is about 200 times slower than the slow component of solvation of the same probe in bulk water.[39] The rotational relaxation study suggests that the probe C480 remains highly mobile within the sol−gel matrix. Pant and Levinger employed femtosecond upconversion to study the solvation dynamics of C343 adsorbed to zirconia particles in water.[67] They observed that the Stokes shift ($\Delta\nu$) is 150 cm^{-1} in zirconia particle which is nearly one-fifth of that (800 cm^{-1}) in water. The solvation time in zirconia particles is 0.24 ps which is similar to that in bulk water.[67]

3.7. Water Surface. Compared to bulk water, the water surface (or more precisely the air−water interface) is different in a number of ways.[68] The average dielectric constant of the water surface has been determined recently and is found to be much smaller than that in the bulk water.[69] Obviously, at the water surface, the solvation energy will be lower than that in the bulk water. At the water surface, the number of solvent

dipoles on the vapor side is quite low. However, if a substantial portion of the probe is dipped inside water, it should experience a bulklike environment. Detailed information on the motion of solvent dipoles in the interfacial region is a subject of great interest. Since, the force experienced by the solute at the water surface is asymmetric, the solvation at the surface depends on the orientation of the solute. Very recently, Eisenthal et al. have studied solvation dynamics of coumarin 314 at the water surface using time-resolved surface second harmonic generation technique.[70] They observed that the solvation dynamics at the water surface depends on the polarization of the pump beam. The solvation time at the water surface is 790 fs for s-polarized and 1200 ps for p-polarized pump beam. The differences in the observed dynamics for pump beams of different polarization is attributed to the existence of different excited solute molecules having different orientations.[70]

4. Origin of the Slow Decay

The most interesting feature of solvation dynamics in restricted environments is the appearance of the slow component of relaxation which is 3−4 orders of magnitude slower compared to that in the corresponding solvent in bulk. It should be emphasized that the solvation dynamics in these complex environments span a very large time scale from sub-100 fs to more than 10 ns; that is at least 5 orders of magnitude! Evidently, if one uses an ultrafast setup and fit the data up to a few picoseconds only, the slow components in the hundreds or thousands of picoseconds time scale will be missed. On the other hand, in a relatively slow setup with time response ≈100 ps, the ultrafast subpicosecond components will go undetected. As a result of this, the experimental and simulation results carried out at different time scales may appear to be in conflict. Evidently, more experiments and simulations taking into account a broad range of time scales will remove the apparent contradictions between different reports. In any case, the existence of a dramatically slow component of solvation has now been established beyond any doubt. It is also obvious that the very diverse time scale of relaxation from sub-100 fs to tens of nanosecond involves different relaxation mechanism. It is unlikely that any one theory can capture all the details.

In general, the magnitude of dynamic retardation in an organized assembly compared to bulk water detected in a solvation dynamic study is much higher than that reported in a NMR study. One should note that the time resolutions of the NMR methods are not fast enough to detect the subpicosecond components of relaxation in bulk water which are readily detected in solvation dynamics studies. Thus, the ratio of relaxation times in an organized assembly and in bulk water determined by NMR is not very accurate. Second, solvation dynamics probes relaxation over a small region, in the immediate vicinity of the solute. However, NMR captures signal from the entire organized assembly. Nevertheless, in many organized assemblies the time scales of relaxation (100−1000 ps) observed in NMR and solvation dynamics are very close.

As noted earlier, the very fast dynamics in bulk water may be attributed to the extended hydrogen bond network and cooperative nature of motion of water.[12] In an organized assembly, the hydrogen-bonded network gets seriously disrupted. In the extreme case of a water molecule buried deep inside a protein, it is not hydrogen bonded to another water molecule and is instead hydrogen bonded to a nearby polar group of the protein. Exchange of such a buried water molecule with bulk water involves rupture of the hydrogen bond with the protein and diffusion out of the protein. This is obviously a very slow process. In the intermediate situation, water is hydrogen bonded to the polar or ionic groups on the surface of the surfactants and the biomolecules. For example, in reverse micelles, the ionic headgroups of the surfactants can make the nearest water molecules nearly immobile. However, these water molecules are certainly not permanently bound to the headgroups and shall undergo slow exchange with the relatively free water molecules inside the water pool. In fact, the dynamic exchange between free and bound water molecules certainly occurs also for proteins and DNAs. The strength of the hydrogen bond to a polar group on the surface of protein can be rather strong. In the dynamic exchange model,[17] the slow relaxation arises as a result of the condition of equilibrium. The dynamic exchange model appears to be valid for many organized assemblies in aqueous solutions.

The effect of the slow time scale (introduced by the dynamic exchange) on the solvation dynamics can be understood in the following way. The time dependent solvation energy is given by the following expression

$$E_{solv}(t) = -\int d\mathbf{r}\, \mathbf{P}(\mathbf{r},t)\cdot\mathbf{E_0}(\mathbf{r},t) \qquad (5)$$

where $\mathbf{P}(\mathbf{r},t)$ and $\mathbf{E_0}(\mathbf{r},t)$ are respectively, the polarization density at position $\mathbf{r}$ at time t and the electric field of the polar species (charge or dipole) at the same position. The polarization density is in turn determined by the position and orientation dependent solvent (here water) density, $\rho(\mathbf{r},\Omega,t)$ where Ω denotes the orientation of a water molecule. The contribution to the polarization density comes primarily from the free molecules which can rotate and translate and, therefore, can respond to the suddenly changed electric field of the probe dipole. The dynamic exchange between the free and the bound water molecules will introduce a slow time scale in $\mathbf{P}(\mathbf{r},t)$ which will be reflected in the solvation dynamics.

There could be an additional, perhaps equally important, source of the slow decay. Since the bound water molecules introduce a structured region extending well into the bulk, there may be a continuum of slow time scales which are bounded by k_{ex}^{-1} and τ_L, where k_{ex} is the sum of the rate constants of the forward and the backward rates in eq 4 and τ_L is the well-known longitudinal relaxation time.

For micelles, one needs to consider the possible contributions from the multipolar interactions between the probe and the charged headgroups of the surfactants. Such multipolar interactions can decay at a rate considerably faster than the dipolar rotation. This possibility may be explored by computer simulation.

The origin of the slow decay in aqueous solutions of cyclodextrin is quite different. When the probe is confined in the cyclodextrin cavity, the few water molecules in its immediate vicinity, i.e., within the cavity, are basically *bound* water. The fact that the initial fast component in the cavity is similar to that in bulk water indicates the initial response is indeed the collective response of the water molecules both inside and outside of the CD cavity.[10,41] The slow component of solvation dynamics detected at long times in cyclodextrin cavity has been attributed to nearly complete loss of the translational degrees of freedom of the bound water which in turn will seriously slow the orientational motion. Actually this is a highly nonlinear process and the existing explanation[41] captures only a part of the story because the quenching of translational motion can affect the rotational motion in more than one ways.

The situation with the microemulsions is again different from both the above cases. In the case of a microemulsion even the

so-called "free" water in the central region of the water pool is not as free as bulk water. This is demonstrated in the compressibility measurements[26] or the static polarity of the big water pool.[30] Even in a large water pool of radius 40 Å, the central water molecules are away from the surfactants only by 15−20 layers of water molecules. The structure of such water can be quite different from that of the bulk, especially for the water within 3−4 layers of the surface. Although the simulations[36] discussed here look promising, they need a lot of refinement to be compared to the experimental results.

The water molecules confined in a self-organized assembly with severely impaired hydrogen-bonded network can be regarded as a liquid in an external field. The occurrence of two vastly different time scales in such systems is a consequence of strong correlation present in liquid water and is due to the existence of both perturbed and unperturbed hydrogen bonds. It will be highly interesting to investigate the temperature dependence of relaxation in confined water and compare the dynamics with that in supercooled water near the glass transition point.

5. Conclusion and Future Outlook

The initial surprise about the discovery of a dramatically slow component in solvation dynamics of water and other liquids in restricted environments has prompted several groups to study this process more closely. However, a comprehensive understanding of the mechanism and implications of this rather general phenomenon is still not available. Since the electron transfer processes in biological systems are controlled by solvation energy, the slow component of solvation energy relaxation in confined media is likely to play an important, hither to unexplored role in biological charge-transfer processes.[20,71]

There are a number of new directions in which the study of dynamics in confined systems may grow. So far there have been only a few attempts to compare dynamics in different regions of a organized assembly by placing the solvation probe at selected locations. As emphasized earlier, the data obtained so far correspond to a region covered by the probe through diffusion. To spatially resolve the dynamics at different regions of these microheterogeneous media, it is necessary to immobilize the probe at selected locations. Study of solvation dynamics with the probe covalently attached to selected sites, should yield such spatially resolved information on dynamics in confined environments. The spatial resolution can be further improved with time-resolved single molecule spectroscopy of such systems. This will give final answer to the question whether the sub-100 fs and the nanosecond components originate from the same region or from the probes confined in different regions. If it could be shown that dynamics in different regions are drastically different, one can then develop more realistic but relatively simpler theoretical models taking into account a smaller segment of the organized medium instead of considering the whole system. Though bulk of the results discussed in this article were obtained using picosecond TDFSS, it is evident that 3PEPS offers a much better time resolution and also has the capability of reporting relaxation over a broad time range. The relaxation behavior of the water around a protein is likely to change during protein folding or on binding of an enzyme to a substrate. To carry out such studies, one needs covalently attached solvation probes which will remain attached to the protein in both folded and unfolded state.

It is astonishing how weak molecular interactions affect structure and dynamics in nature. As shown in this article replacement of water−water hydrogen bonds by water-macromolecule hydrogen bonds lead to profound changes in the dynamics. Such replacement involve small differences in energy. However, this replacement destroys the water−water hydrogen bond network and couples the motion of the small water molecule with the slow moving macromolecules. This causes such marked changes in the dynamics in restricted environments. The future challenge is not only to unravel the microscopic reason for such dramatic changes but also to explore the role of the slow component in biological processes.

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