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Solvation dynamics in organized assemblies. 4-Aminophthalimide in micelles

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Solvation dynamics of 4-aminophthalimide (4-AP) has been studied in neutral (triton X-100, TX), cationic (cetyl trimethyl ammonium bromide, CTAB) and anionic (sodium dodecyl sulfate, SDS) micelles using picosecond time resolved Stokes shift. Above critical micellar concentration (CMC), for all the three micelles, 4-AP exhibits wavelength dependent fluorescence decays with a fast decay at the blue end and a slow decay accompanied by a distinct growth at the red end of the emission spectra. The time dependent Stokes shift indicates that the water molecules in the Stern layer of the micelles relax in ≈100 ps time scale which is markedly slower than the subpicosecond relaxation dynamics observed in ordinary bulk water. © 1998 Elsevier Science B.V.

1. INTRODUCTION

Study of solvent relaxation constitutes one of the most active area of research in contemporary physical chemistry [1-33]. Over the last decade, the intense activity, in this area, has unraveled the early events of the solvation dynamics in many homogeneous solutions and binary liquid mixtures. However, the more complex microheterogeneous systems and organized assemblies remain vastly unexplored. Relaxation behaviour of the water molecules, bound to various organized assemblies and perturbed by local electrostatic and hydrogen bond interactions, is of fundamental importance to understand many natural and biological processes occurring in confined environments. Very recently, several groups have addressed this issue [7, 12, 29-33]. Fleming *et al.* first studied solvation dynamics of coumarin 480 in γ-cyclodextrin (γ-CDx) [7]. They showed that while in ordinary bulk water the solvation occurs in the sub-picosecond timescale (310 fs), in γ-CDx the solvation dynamics exhibits a component in the nanosecond timescale. Nandi and Bagchi ascribed the retardation of the solvation process in cyclodextrin cavity to the

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freezing of the translational modes of the water molecules inside the cavity [12]. The recent dielectric relaxation and NMR studies [34-38] also showed that while ordinary water molecules relax in the time scale of a few ps, living tissues and other biological materials exhibit broadly two relaxation times, one around 10 ps and the other around 10 ns. To explain the almost universally observed bimodal relaxation behaviour of the organized and biological assemblies, the early workers used a rather simplified model involving two kinds of water, "free" and "bound", relaxing in the pico- and nanosecond time scale, respectively. Very recently, Nandi and Bagchi proposed a more rigorous model which envisages an equilibrium between the "free" and the "bound" water where the nanosecond component arises not because of the slowness of the bound water but due to the need for the establishment of an equilibrium [13].

Inspired by these studies, we have recently initiated a systematic investigation on the solvation dynamics in several organized assemblies [29-32]. In the solid host, zeolite 13X, solvation of coumarin 480 is observed to occur in the nanosecond timescale [29]. Again, in a microemulsion, the water molecules relax in the nanosecond timescale [30,32]. The microemulsions, refer to water droplets ("water pool"), surrounded by a layer of surfactant and dispersed in a hydrocarbon solvent. The radius of the water pool may be varied from a few Å to nearly 100 Å by varying the ratio of the number of the water and the surfactant molecules. It is observed that in the small water pools ($r < 10$ Å) the solvation time is about 8 ns while in the big water pools the solvation time decreases to about 2 ns [30, 32-33]. In the water pool of the microemulsions, the solvation times of two probes, 4-aminophthalimide (4-AP) and coumarin 480 (C-480), are found to be of similar magnitude [30, 32]. Nanosecond solvation dynamics in microemulsions is also reported by Bright *et al.* [33]. Using phase fluorimetry, they studied solvation of a biological fluorophore covalently attached to albumin. More recently, it is reported that C-480 exhibits subnanosecond solvation dynamics in several micelles [31]. The surfactants, triton X-100 (TX), cetyl trimethyl ammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) form nearly spherical micellar aggregates when their concentrations exceed certain critical value, known as the critical micellar concentration (CMC). Each of such aggregates contains 100-150 surfactant molecules with a radius of around 50 Å for TX and CTAB and 30 Å for SDS. Recent small angle X-ray [40] and neutron scattering [41-43], NMR and other techniques [39] have revealed detailed information on the structure of these micelles. According to these studies, the core of the micelles is essentially "dry" and consists entirely of the hydrocarbon chains. At the periphery of the micelles, there is a "wet" shell, of thickness 6-9 Å for CTAB and SDS, comprising of the polar headgroup, the counterion and considerable amount of water [41-43]. This shell, known as the Stern layer, is quite polar though it is obviously not as polar as bulk water. Small angle X-ray scattering of triton X-100 micelles indicates the presence of a hydrophobic portion of radius 25-27 Å, surrounded by a hydrophilic shell of thickness 25 Å so that total radius is about 51 Å [40]. In the micellar system, the probe solute may reside in three different environments, the highly polar bulk aqueous phase, the hydrocarbon core and the Stern layer. In our earlier studies on C-480, we could not ensure the presence of the probe exclusively in the Stern layer as it is highly soluble in hydrocarbon solvents and hence, a major portion of it stays in the hydrocarbon core. Still, we could study solvation dynamics selectively at the Stern layer as C-480 does not exhibit wavelength dependent fluorescence decays in *n*-heptane

and hence, those C-480 molecules, at the hydrocarbon core, are not expected to exhibit solvation dynamics while for those probe molecules, present in the bulk aqueous phase, the solvation dynamics is too fast (< 1 ps) to be detected in our picosecond setup (resolution about 50 ps). Another solvation probe 4-aminophthalimide (4-AP), however, stays preferentially at the Stern layer and does not penetrate the hydrocarbon core because it is insoluble in hydrocarbon solvents. The concentration of 4-AP in bulk aqueous phase is very small at very high surfactant concentration when most of the probe molecules are bound to the micelles. The concentration of the micelles needed for 90% binding may be estimated from the reported binding constant of 4-AP with these micelles [44]. In the present work, we have tried to answer how the solvation dynamics in micelles depends on the probe by studying 4-AP in micelles. The extreme sensitivity of 4-AP to hydrogen bonding solvents has been the subject of several recent studies and has recently been utilised to monitor the micellisation process [28, 32, 44-47].

2. EXPERIMENTAL

The single photon counting setup and the laser system is described elsewhere [29-32]. Triton X-100 (Aldrich) was used as received. Other surfactants (Aldrich) and 4-AP (Kodak) were purified by recrystallisation. The wavelength of excitation for steady state and time resolved studies is 305 nm. The fluorescence decays were recorded at intervals of 15 nm using a Corning 3-74 filter (to cut-off scattered laser light) and a slitwidth less than 5 nm. The decays were fitted to a single or a bi-exponential decay using global lifetime analysis software (PTI). Reconstruction of the time resolved spectra was done following the procedure described by Maroncelli and Fleming [6]. Briefly, the fluorescence intensities were normalised using the steady state emission spectrum. Then using the parameters of the best fit to the fluorescence decays, time resolved spectra at different time, t, were generated by fitting the data to a log-normal function to get the peak frequency $\nu(t)$. The peak frequency at infinite time $\nu(\infty)$ refers to the peak frequency at very long time when the spectrum no longer exhibits any time dependent Stokes shift.

3. RESULTS AND DISCUSSION

3.1 Steady State Spectra:

In aqueous solution, 4-AP exhibits a very weak emission (ϕ_f=0.01) with maximum at around 550 nm [43-44]. On addition of surfactants, to an aqueous solution of 4-AP, the emission intensity and lifetime of 4-AP remain more or less unchanged until the concentration of the surfactants reach the CMC. Above CMC, the fluorescence quantum yield and lifetime of 4-AP increase abruptly (about 3 times) and the emission maximum exhibits a distinct blue shift of about 20 nm which indicates that the probes are transferred from the polar aqueous phase to the less polar micellar region [44]. From the position of the emission maxima, the static polarity of the micelles are inferred to be of the order SDS > CTAB > TX [44]. However, it should be pointed out that the probe 4-AP molecule scans

a region of space within its lifetime of a few ns. If it is assumed that the diffusion coefficient of the probe is similar to those of ordinary organic molecules in water (0.5 $Å^2ps^{-1}$) the probe diffuses about 1 nm per ns [48]. Thus the micropolarity, reported by the emission maximum of 4-AP, corresponds to a region of radius of a few nm.

3.2 Time Resolved Studies:

In an earlier study, Saroja and Samanta reported that the fluorescence lifetime of 4-AP remains more or less same upto the CMC and then increases as the probe binds to the micellar aggregates [44]. However, in their nanosecond setup they could not detect the time dependent Stokes shift. To eliminate the contribution of free 4-AP present in bulk water, we used very high concentration of the surfactants (180 mM for CTAB, 160 mM for SDS and 180 mM for TX). At these concentrations, about 90% of the probe 4-AP molecules remain bound to the micelles. It is observed that under such a condition the fluorescence decays at the red end differ significantly from those at the blue end (fig. 1). The decay at the red end exhibits a distinct growth. For instance, in 180 mM TX the decay at 620 nm could be fitted to a biexponential with a growth component of 1.17 ns and a decay component of 4.6 ns while at 450 nm one observes only a decay of 1.3 ns lifetime. Such a wavelength dependent emission decay indicates a time dependent Stokes shift of the emission spectra. In this case, the energy of the probe dipole continuously decreases with time due to solvation causing a decay at the blue end and a growth at the red end of the emission spectra.

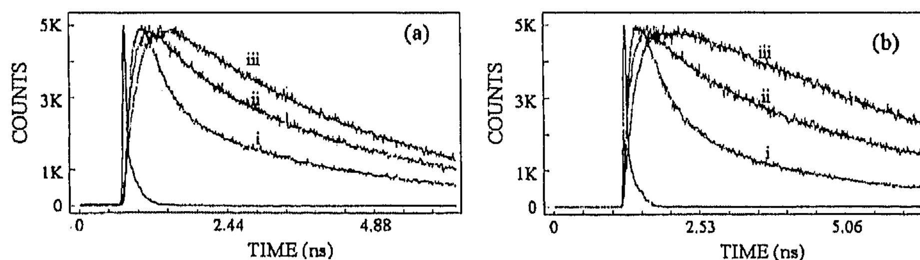

Figure 1. Fluorescence decays of 4-AP in (a) 180 mM CTAB at (i) 460, (ii) 490 and (iii) 600 nm and (b) 180 mM TX at (i) 450, (ii) 495 and (iii) 600 nm.

In order to get detailed information on the solvation dynamics, the time resolved emission spectra of 4-AP in aqueous solutions, in the presence of the surfactants above CMC, are constructed at different times from the decays recorded at different wavelengths (fig 2). In this case, the contribution of the emission of 4-AP in the hydrocarbon core and in bulk water can be neglected as 4-AP is insoluble in the hydrocarbon core and as there are very few (10 %) free 4-AP molecules with very low emission quantum yield in bulk water. Fig. 2 describes the time resolved emission spectra of 4-AP in CTAB and TX micelles. The reconstructed response function C(t), defined as,

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

were calculated using the peak frequencies $\nu(\infty)$, $\nu(t)$ and $\nu(0)$ at times ∞, t and 0, respectively. The time constant of the solvation dynamics in the Stern layer of the micelles is obtained from the temporal dependence of C(t). Fig. 3 shows the decay of C(t) and table 1 summarises the decay characteristics of C(t) for the three micelles.

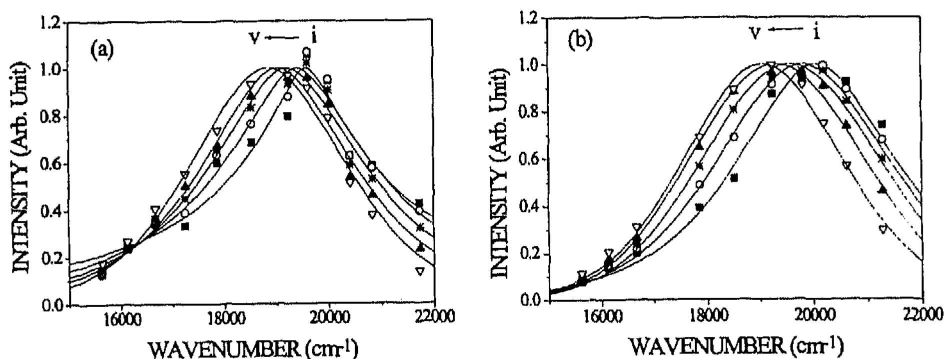

Figure 2. Time resolved emission spectra of 4-AP in (a) 180 mM CTAB, at (i) 0 (■), (ii) 50 (O), (iii) 150 (∗), (iv) 350 (▲) and (v) 2000 (∇) ps and (b) 180 mM TX, at (i) 0 (■), (ii) 150 (o), (iii) 350 (∗), (iv) 850 (▲) and (v) 4000 (∇) ps.

For the three micelles the average solvation times $\langle\tau\rangle$, defined as $\Sigma a_i\tau_i$, are 82, 273 and 716 ps, respectively for SDS, CTAB and TX. It may be recalled that in our previous study on C-480, we observed that for SDS the solvation dynamics is dominated by a major component of 180 ps while for CTAB and TX, $\langle\tau\rangle$ are 474 and 1456 ps, respectively. In the previous study, not only was the probe different but the micelle concentrations were at least one order of magnitude lower. In spite of these, the solvation times for 4-AP and C-480 differ only by a factor of two which suggests that the solvation dynamics in the Stern layer of the micelles does not depend very strongly on the probe.

Table 1
Decay characteristics of C(t) of 4-AP in different micelles.

Surfact.	concn. (mM)	$\Delta\nu$ (cm^{-1})	a_1	τ_1 (ps)	a_2	τ_2 (ps)	$\langle\tau\rangle$ (ps)
SDS	160	1043	1.0	82	—	—	82
CTAB	180	740	0.39	100	0.61	383	273
TX	180	1000	0.59	331	0.41	1270	716

The solvation dynamics, in the Stern layer of the micelles, is nearly three orders of magnitude slower than the solvation dynamics (310 fs) reported by Fleming *et al.* in bulk water [7], about ten times faster than the solvation dynamics observed in the water pool of the reverse micelles [30, 32-33] and is slightly faster than that reported in the case of γ-CDx [7]. The main candidates causing solvation of the instantaneously created dipole, in this case, are the polar head groups of the micelles and the water molecules. The mobility of the polar head groups is restricted to a very large extent as they are tethered to the long alkyl chains and the chain dynamics of polymers occur in a much slower time scale of 100 ns [49]. Thus we ascribe the solvation dynamics in the 82-716 ps time scale, for 4-AP in micelles, to the water molecules present in the "wet" Stern layer of the micelles. For the neutral micelle, TX, evidently the only candidates for solvation are the water molecules present in the Stern layer. However, for the ionic micelles (SDS and CTAB) the counterions may also contribute to the solvation dynamics. However, the effectively stationary ionic headgroups of the surfactants also render the counterions quite immobile.

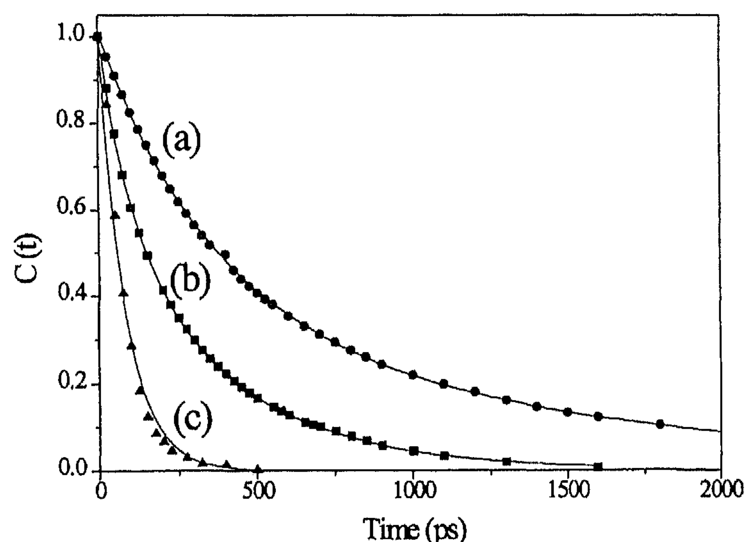

Figure 3. Decays of the response function, C(t) of 4-AP in (a) 180 mM TX, (b) 180 mM CTAB and (c) 160 mM SDS . The points denote the actual values of C(t) and the solid line denotes the best fit to a single or bi-exponential decay.

Thus the role of ionic solvation appears to be minor, in this case. The non-exponential decay of C(t) may arise from the inhomogeneity in the immediate neighbourhood of the probe. To explain the non-exponential solvation dynamics in the homogeneous solutions, Castner *et al.* earlier used an "inhomogeneous continuum" model assuming a dielectric constant $\varepsilon_0(r)$, dependent on distance, r, from the probe [8]. Application of this model involves assumption of a particular mathematical form for $\varepsilon_0(r)$ since $\varepsilon_0(r)$ can not be determined experimentally. Such a procedure is very difficult to apply to the present

complex system of micelles, involving many components such as surfactants, counterions and water. Thus at this stage, we refrain from quantifying the result.

The solvation times are of the order TX > CTAB > SDS. Qualitatively, the difference in the solvation times arises from the differences in the structure of the micelles. As mentioned earlier, thickness of the hydrated shell (Stern layer) for TX (25 Å) is much higher than those for SDS and CTAB (6-9 Å) [40]. Thus while the probe is surrounded by one or two layers of solvent (water) in the Stern layer, for SDS and CTAB, there are many such layers for TX. Between the Stern layer and bulk water, there is a diffuse and loose layer, called the Guoy-Chapman (G.C.) layer, where the water molecules are expected to move much faster compared to the Stern layer [44]. For SDS and CTAB, the probe 4-AP molecule remains very close and partially exposed to the G.C. layer while in the case of TX the probe is well shielded from the G.C. layer. Since the G.C. layer is expected to exhibit faster relaxation dynamics, CTAB and SDS show faster solvation dynamics compared to TX. The small angle neutron scattering studies indicate that CTAB micelles are drier than SDS micelles. Thus the faster solvation times in SDS, compared to CTAB, may be ascribed to the more water like environment in SDS.

4. CONCLUSION

4-AP exhibits time dependent Stokes shift, in neutral, cationic and anionic micelles. The solvent relaxation times in the micelles, for 4-AP, differ from those obtained with coumarin 480 only by a factor of two. This suggests that the solvation dynamics, in the micelles, depends weakly on the probe. The main species, responsible for the solvation in the micelles, are the water molecules present in the Stern layer of the micelles. The time constant of the solvation dynamics indicates that the water molecules in the Stern layer are much slower than those in bulk water but are faster than the highly structured water molecules present in the water pool of the reverse micelles. It may be noted that the various organized media retard not only the solvation dynamics but also other ultrafast processes, e.g. twisted intramolecular charge transfer [48, 50-53] and photoisomerisation [54-55]. However, while the solvation dynamics is slowed down several thousand times, the magnitude of retardation, caused to the other processes, is much lower.

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