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Hydration dynamics of 4-aminophthalimide in a substituted β-cyclodextrin nanocavity

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Abstract

Solvation dynamics of water molecules around a probe, 4-aminophthalimide (4-AP) inside a heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin (TRIMEB) cavity has been studied using picosecond time dependent fluorescence Stokes' shift. The solvation time of 4-AP within the TRIMEB cavity in water is found to be 250 ± 50 ps. This is substantially slower than the solvation time observed in bulk water (∼1 ps).

Keywords: Fluorescence; Stokes shift; Lifetime; Slow solvation dynamics; Methyl cyclodextrins

1. Introduction

Dynamics in confined environments is of fundamental importance to understand the structure and reactivity in complex biological systems [1–5]. In bulk water, solvation dynamics is extremely fast [6–8]. Using several coumarin dyes as a probe, it has been shown that solvation dynamics in bulk water is described by a major component in 0.1 ps time scale and a minor component of ∼1 ps [7,8]. Most recently, it is reported that in confined environments water exhibit a 100–1000 ps component which is slower by 2–3 orders of magnitude compared to bulk water [9–19].

Perhaps, the most well characterized example of a confined liquid, is the water molecules entrapped inside a nanocavity of a cyclodextrin. A cyclodextrin molecule possesses a nanocavity of height ∼8 Å and diameter 4.5, 6.5 and 8 Å for α-, β-, and γ-cyclodextrin, respectively, and may encapsulate a guest molecule along with several solvent molecules [20]. The interior of a cyclodextrin cavity resembles a cyclic ether and is hydrophobic in nature. Structures of inclusion complexes comprising cyclodextrin as a host and an organic guest molecule along with several solvent molecules have been studied in great detail [21–23].

So far, only two time dependant fluorescence Stokes' shift studies have been reported for a cyclodextrin [18,19]. Vajda et al. studied solvation dynamics of water confined in a γ-CD cavity using coumarin 480 as a probe [18]. They observed that inside the γ-CD cavity the solvation dynamics exhibits a very slow component. The slow dynamics in γ-CD is described by three components of 13, 109 and 1200 ps, respectively [18]. We had previously reported that solvation dynamics of 4-aminophthalimide (4-AP) in a β-cyclodextrin (β-CD) cavity in a non-aqueous solvent (DMF) is described by a component of 400 ± 50 ps (25%) and another slow component of 8000 ± 1000 ps (75%) [19]. This is substantially slower than the solvation time (∼1 ps) in bulk DMF. Nandi and Bagchi attributed the slow component to almost complete suppression of the translational modes of the confined water molecules within the cyclodextrin cavity [10].

There is no report on solvation dynamics in a substituted cyclodextrin. In this work, we report on the solvation dynamics of 4-aminophthalimide (4-AP) in aqueous solution containing heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin

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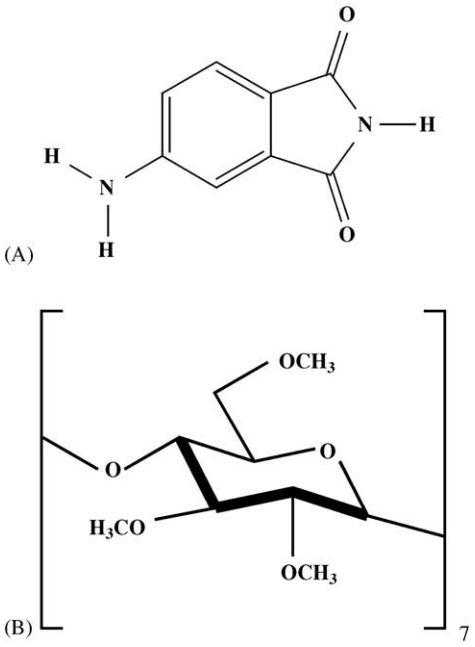
(TRIMEB). In TRIMEB all the secondary hydroxyl hydrogens of the cyclodextrin are substituted by methyl groups. The methyl substituted cyclodextrins are generally more soluble than the unsubstituted ones. The non-availability of hydroxyl groups at the rim of such a substituted cyclodextrin excludes the possibility of hydrogen bonding with the carbonyl groups of 4-AP molecule.

2. Experimental

4-Aminophthalimide (4-AP, Scheme 1A) was purchased from Kodak and was purified by repeated recrystallization from methanol-water mixture. Heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin (TRIMEB, Fluka, Scheme 1B) were used as received. The steady-state absorption and emission spectra were recorded in a Shimadzu UV-2401 spectrophotometer and a Spex, FluoroMax-3 spectrofluorimeter, respectively.

For lifetime measurements, the samples were excited at 375 nm using a picosecond diode laser (IBH Nanoled-07) in an IBH Fluorocube apparatus. The emission was collected at a magic angle polarization using a Hamamatsu MCP photomultiplier (5000U-09). The time correlated single photon counting (TCSPC) setup consists of an Ortec 9327 CFD and a Tennelec TC 863 TAC. The data is collected with a PCA3 card (Oxford) as a multi-channel analyzer. The typical FWHM of the system response using a liquid scatterer is about 100 ps. The fluorescence decays were deconvoluted using IBH DAS6 software. All experiments are carried out at 22 °C.



Scheme 1. (A) Structure of 4-aminophthalimide (4-AP). (B) Structure of heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin (TRIMEB).

3. Results

3.1. Steady-state absorption and emission

In water, the lowest energy absorption bands of 4-AP appear at 370 and 300 nm. Of these, the 370 nm band is $n\pi^*$ in nature and the 300 nm band contains contribution of $\pi\pi^*$ transition [23–25]. On addition of heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin (TRIMEB), the absorbance of 4-AP at 370 nm remains unchanged, while the absorbance at 300 nm increases with TRIMEB concentration (Fig. 1).

Emission maximum of 4-AP is very sensitive to polarity of the environment [23–25]. In water, 4-AP exhibits an emission maximum at 550 nm with emission quantum yield (ϕ^f) of 0.014 [23,24]. On addition of TRIMEB to water, the emission maximum of 4-AP undergoes a dramatic blue shift and a marked increase in the emission intensity (Fig. 2). At 50 mM TRIMEB, 4-AP exhibits an emission maximum at 507 nm (i.e. blue shifted by 43 nm from that in bulk water) with an emission quantum yield (ϕ^f) of 0.11 which is nearly eight times larger compared to that in water. It may be recalled that the emission peak of 4-AP in unsubstituted β-CD is at 513 nm [23] which is 6 nm red shifted from that in TRIMEB. The red shift of the emission spectrum of 4-AP in unsubstituted β-CD may be because of the hydrogen bonding between 4-AP with the secondary hydroxyl groups of the unsubstituted β-cyclodextrin.

The binding constant (K_b) of 4-AP to TRIMEB corresponds to the following equilibrium:

$$\text{4-AP} + \text{TRIMEB} \rightleftharpoons [\text{4-AP : TRIMEB}] \quad (1)$$

The value of K_b may be determined from the changes in absorption and emission spectra as described by Hoshino et al. [26]. If A_0, A_C, and A_∞ denote absorbance of 4-AP at a

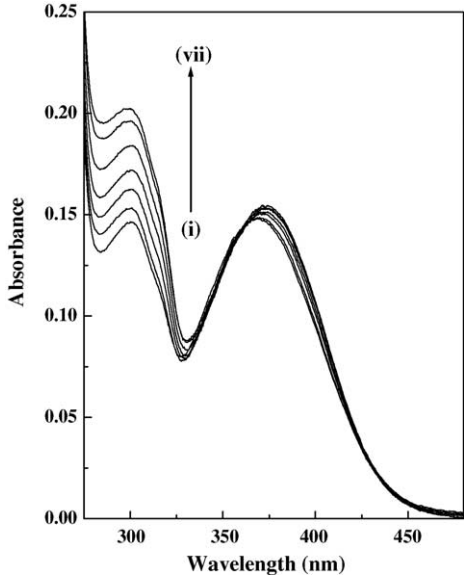


Fig. 1. Steady-state absorption spectra of 4-AP in water in the presence of 0, 3, 10, 20, 30, 40 and 50 mM TRIMEB, respectively ((i) → (vii)).

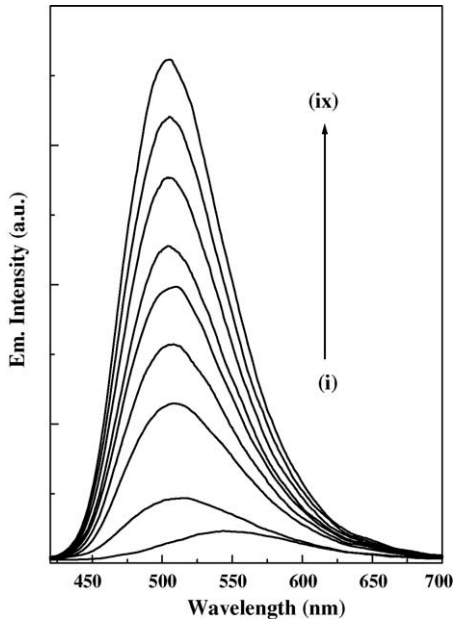


Fig. 2. Steady-state emission spectra of 4-AP in water in the presence of 0, 3, 6, 10, 15, 20, 30, 40 and 50 mM TRIMEB, respectively ((i) → (ix)).

wavelength λ (300 nm in this case) at a cyclodextrin concentration 0, C_{CD} and infinity, according to Hoshino et al. [26]:

$$\frac{A_C - A_0}{C_{CD}} = K_b(A_\infty - A_C) \tag{2}$$

Fig. 3 shows a plot of $\frac{A_C - A_0}{C_{CD}}$ versus A_C. From the slope K_b is found to be $50 \pm 5\,M^{-1}$ for 4-AP in TRIMEB–water system.

In the case of emission, at any concentration of cyclodextrin, the observed emission quantum yield (ϕ) contains contribution from both free (ϕ^f) and bound (ϕ^b) 4-AP. Thus

$$\phi = \frac{\phi^f I^f + \phi^b I^b}{I^f + I^b} \tag{3}$$

where $I^{f(b)}$ denotes intensity of light absorbed by the free (bound) probe. If $\Delta\phi$ is the difference in emission quantum yield of 4-AP in water in the absence of TRIMEB with that at a cyclodextrin (TRIMEB) concentration C_{CD}, then according to Hoshino et al. [26]:

$$\frac{1}{\Delta\phi} = \frac{(\phi^b - \phi^f)^{-1} + (\phi^b - \phi^f)^{-1}\varepsilon^f}{K_b \varepsilon^b C_{CD}} \tag{4}$$

where $\varepsilon^{f(b)}$ denotes molar extinction coefficient of free (bound) probe. At an excitation wavelength (e.g. ~390 nm for 4-AP) where $\varepsilon^b \approx \varepsilon^f$, the double reciprocal plot of $\Delta\phi$ against concentration of TRIMEB (Fig. 4) yields the value of K_b from the ratio of intercept and slope. In 4-AP-TRIMEB–water system the value of K_b is determined to be $45 \pm 2\,M^{-1}$.

It is evident that binding constant of 4-AP to methyl substituted β-CD (TRIMEB) is about four times smaller than that with unsubstituted β-CD ($208\,M^{-1}$ [23]). One possible reason for the lower binding constant in methyl substituted, TRIMEB (compared to unsubstituted β-CD) may be the non-availability of hydroxyl groups in TRIMEB to form hydrogen bond with the carbonyl groups of 4-AP.

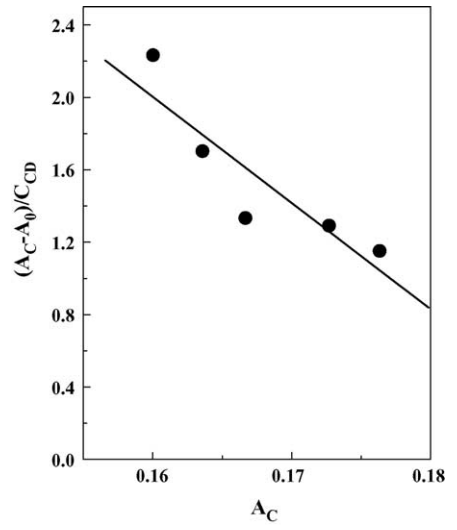


Fig. 3. Plot of $\frac{A_C - A_0}{C_{CD}}$ vs. A_C for 4-AP in water with varying TRIMEB concentration. The points represent experimental values and the solid line represents the best linear fit to the data.

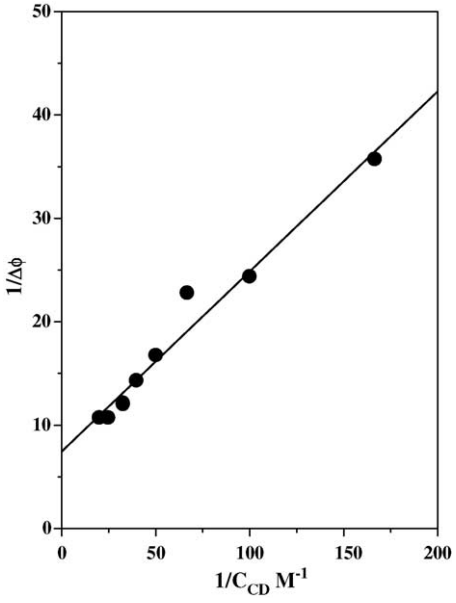


Fig. 4. Plot of $\frac{1}{\Delta\phi}$ vs. $\frac{1}{C_{CD}}$ for 4-AP in water with varying TRIMEB concentration. The points represent experimental values and the solid line represents the best linear fit to the data.

3.2. Time resolved studies

In water, 4-AP exhibits an emission decay with a life time of 1.2 ns [27]. Solvation dynamics in bulk water occurs in <1 ps time scale, and is thus too fast to be detected in a picosecond setup of time resolution ~100 ps. Hence, the

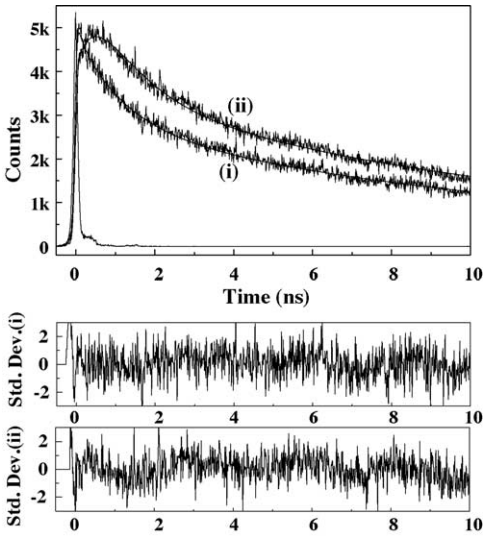


Fig. 5. Fluorescence decays of 4-AP in 50 mM TRIMEB in water at (i) 450 nm ($\chi^2 = 1.13$) and (ii) 570 nm ($\chi^2 = 1.10$) along with the distribution of residuals.

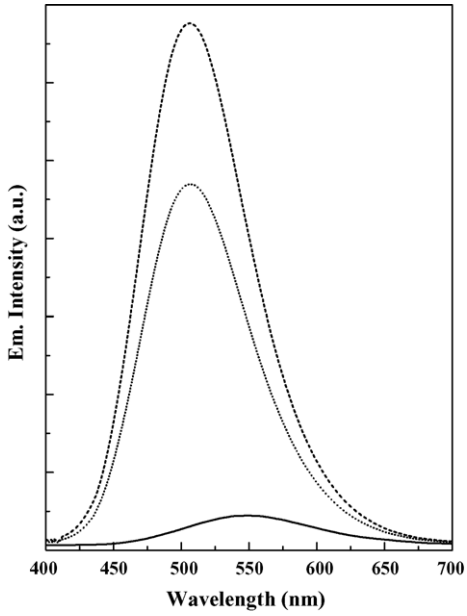


Fig. 6. Emission spectrum of 4-AP (i) in water (—), (ii) in 50 mM TRIMEB in water (···), (iii) bound to TRIMEB in water (- - -) (calculated as described in text).

fluorescence decays of 4-AP in water are independent of the emission wavelength.

In the presence of TRIMEB, significant wavelength dependence of fluorescence decays of 4-AP is observed even in a picosecond setup. In the presence of 50 mM TRIMEB in water, the fluorescence of 4-AP displays a decay at the blue end while at the red end the decay is preceded by a growth. For example, the decay of emission of 4-AP at the blue end (450 nm) is fitted to a tri-exponential function with 2.4 ns (2400 ps) and 12.8 ns along with a 1.2 ns (1200 ps) bulk water like component (corresponds to free 4-AP molecules). However, at the red end (570 nm) the decay is fitted to a tri-exponential function with a 12.2 ns decay component and a 0.44 ns (440 ps) rise component (along with a decay of 1.2 ns bulk water like component) (Fig. 5). The decay components of 4-AP in 50 mM TRIMEB at different wavelengths are given in Table 1. Such a wavelength dependence of emission decays indicate that in TRIMEB cavity, 4-AP exhibits solvation dynamics in a time scale much slower than the solvation dynamics observed in neat water (∼1 ps).

4. Discussion

It should be emphasized that in 50 mM TRIMEB in water, a significant amount of 4-AP remains in the free form in bulk water. Thus, in order to extract the solvation dynamics of 4-AP bound to TRIMEB it is necessary to subtract the contribution of the free 4-AP in water both from the steady state and the time resolved emission data.

The contributions of free and bound 4-AP to the steady-state emission spectra in the presence of 50 mM TRIMEB may be determined as follows. According to the value of K_b determined in this work, at a concentration of 50 mM TRIMEB in water, 68 ± 2% 4-AP remain in the bound from. Thus, the observed emission intensity may be expressed as

$$I_{obs}(\lambda, t) = 0.68 I^{b}_{ss}(\lambda, t) + 0.32 I^{f}_{ss}(\lambda, t) \quad (5)$$

where $I^{b}_{ss}(\lambda, t)$ and $I^{f}_{ss}(\lambda, t)$ represent the contributions of respectively bound and free 4-AP molecules, to the steady-state emission intensity at an emission wavelength λ.

The emission spectrum due to 4-AP molecules bound to TRIMEB is obtained by subtracting the contribution of free 4-AP in bulk water (32 ± 2%) from the total emission spectrum in 50 mM TRIMEB in water. This is shown in Fig. 6. The emission maximum of 4-AP bound to TRIMEB is observed to be at 507 nm with emission quantum yield (ϕ_f) of 0.15.

The contribution of free and bound 4-AP to the temporal decay may be accounted for as follows. At all wavelengths, the fluorescence decay of 4-AP in 50 mM TRIMEB were found to be tri-exponential function with a 1.2 ns (1200 ps) bulk water like component (τ_3) along with two other components. While the other two components were invariably due to 4-AP bound to TRIMEB, the 1.2 ns component contains contribution from both bound and free 4-AP. At any wavelength λ, the decay of the emission of 4-AP bound to β-CD is given by

$$I^{b}(\lambda, t) = \frac{I^{b}_{SS}(\lambda)}{\sum_i b_i \tau_i}[b_1 e^{-t/\tau_1} + b_2 e^{-t/\tau_2} + b_3 e^{-t/\tau_3}] \quad (6)$$

where $I^{b}_{SS}(\lambda)$ denotes the steady-state intensity due to bound 4-AP and $b_1 + b_2 + b_3 = 1$. In 50 mM TRIMEB, 32% of 4-AP molecules exist in the free form and display a single exponential decay of life time 1.2 ns and the rest (68%) of 4-AP molecules remain in the bound form. Thus, the observed

Table 1
Fluorescence decay parameters of 4-AP in 50 mM TRIMEB in water

λ_{em} (nm)	b_1 (a_1)[a]	τ_1 (ps)[a]	b_2 (a_2)[a]	τ_2 (ps)	b_3 (a_3)[a]	τ_3 (ps)[a]
450	0.14 (0.12)	2400	0.38 (0.46)	1200	0.48 (0.42)	12800
470	0.14 (0.12)	3930	0.09 (0.21)	1200	0.77 (0.67)	13700
485	0.26 (0.22)	5800	0.02 (0.16)	1200	0.72 (0.62)	15400
495	−0.63 (−0.45)	350	0.22 (0.39)	1200	1.41 (1.06)	12800
505	−0.85 (−0.62)	320	0.22 (0.43)	1200	1.63 (1.20)	12900
520	−0.83 (−0.56)	350	0.21 (0.46)	1200	1.62 (1.10)	12900
535	−1.48 (−0.81)	380	0.43 (0.68)	1200	2.05 (1.12)	12800
550	−1.78 (−0.79)	390	0.48 (0.77)	1200	2.30 (1.03)	12500
570	−2.76 (−0.87)	440	0.91 (0.97)	1200	2.85 (0.90)	12200
590	−4.06 (−0.84)	470	1.30 (1.06)	1200	3.76 (0.78)	12000

a_i's are the experimentally obtained amplitudes of decay time constants, b_i's are the calculated values of the corresponding amplitudes of decay time constants for 4-AP bound to TRIMEB.
[a] ±10%.

temporal decay [$I_{obs}(\lambda, t)$] may be expressed as

$$I_{obs}(\lambda, t) = 0.68\frac{I^{b}_{SS}(\lambda)}{\sum_i b_i\tau_i}b_1\,e^{-t/\tau_1} + 0.68\frac{I^{b}_{SS}(\lambda)}{\sum_i b_i\tau_i}b_2\,e^{-t/\tau_2} + \left[0.32\frac{I^{f}_{SS}(\lambda)}{\tau_3} + 0.68\frac{I^{b}_{SS}(\lambda)}{\sum_i b_i\tau_i}b_3\right]e^{-t/\tau_3} \quad (7)$$

From the ratio of steady-state emission intensities of bound and free form (I^{b}_{SS}/I^{f}_{SS}) from Fig. 6 and from the amplitudes of the tri-exponential decay components, one can obtain the amplitudes of the decay components (b_i) for the bound form. Then the time resolved emission spectra (TRES, Fig. 7) are constructed following the method of Maroncelli and Fleming [28]. The solvation dynamics is described by the decay of the solvent response function $C(t)$, defined by

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \quad (8)$$

where $\nu(0)$, $\nu(t)$ and $\nu(\infty)$ are the emission frequencies at time zero, t and infinity. The decay of $C(t)$ for 4-AP in 50 mM TRIMEB in water is shown in Fig. 8. It is readily seen that decay of $C(t)$ is purely single-exponential with decay constant of 250 ± 50 ps. The observed time-dependent Stokes' shift is 950 ± 50 cm^{-1}.

It is obvious that, the hydration dynamics of 4-AP in 50 mM TRIMEB is much slower than that in bulk water. There could be many reasons for the slowing down of solvation dynamics in cyclodextrin cavity. The hindered water molecules inside the nano-vessel may be responsible for the slow solvation dynamics. As noted earlier, Nandi and Bagchi [10] ascribed the slow components of solvation dynamics

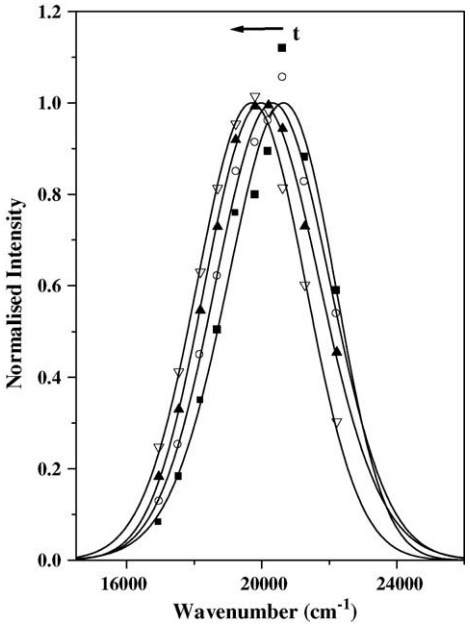


Fig. 7. Time resolved emission spectra of 4-AP bound to TRIMEB in water at 0 ps (■), 150 ps (○), 300 ps (▲) and 1500 ps (▽).

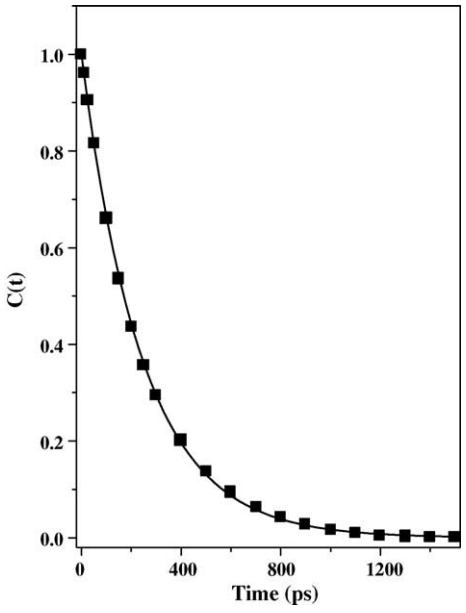


Fig. 8. Decay of response function, $C(t)$ of 4-AP bound to TRIMEB in water. The points denote the actual values of $C(t)$ and the solid line denotes the best fit to an exponential decay.

of water in γ-CD cavity to the freezing of the translational modes of the solvent inside the nanocavity of cyclodextrin. One might argue that motion of the probe molecule (4-AP) in and out of the cavity may also give rise to the slow component. However, a recent study shows that the slow dynamics of entry and exit from a CD cavity occurs in 100 ns time scale [29]. This is too slow to explain the observed 0.25 ns (250 ps) time constant of solvation in the TRIMEB cavity. Such a self diffusion of a probe gives rise to time dependent decay of spectral width [30]. However, in the case of TRIMEB the change in the spectral width is found to be very small (<10%) for 4-AP in TRIMEB. Thus it seems that self-motion of probe plays a small role in this case.

The slow solvation dynamics observed in cyclodextrin and other self-organized assemblies (e.g. micelle, proteins) may also arise from an exchange of "bound" and "free" water as proposed by Nandi and Bagchi [11]. According to this model the water molecules in the first solvation shell of cyclodextrin (or a protein or micelle) are almost immobilized because of hydrogen bonding with the cyclodextrin (or other biological assemblies). This water molecules are referred to as "bound" water. The water molecules at distance are hydrogen bonded to only water molecules and retain bulk water like mobility. These water molecules are called "free". In the limit of high binding energy ($G_{\text{bound}} < G_{\text{free}}$) the slow component of solvation is given by

$$\tau_{\text{slow}} \approx k_{\text{bf}}^{-1} \tag{9}$$

where k_{bf} denotes the rate constant for bound-to-free interconversion. In this model

$$k_{\text{bf}} = \left(\frac{k_{\text{B}}T}{h}\right) \exp\left(-\frac{|\Delta G_{\text{bf}}^{\circ}| + \Delta G^{*}}{RT}\right) \tag{10}$$

where ΔG^{*} is the activation energy for the conversion of free-to-bound water molecules. Using the time constant of slow solvation (250 ps) the binding energy ($|\Delta G_{\text{bf}}^{\circ}|$) in TRIMEB–water system is 3.4 Kcal mol^{-1}.

5. Conclusions

The present work describes the water dynamics inside the methoxy substituted cyclodextrin (TRIMEB) nanocavity using 4-AP as a solvation probe. From steady-state measurement, it has been found that about 70% of probe molecules are bound to the TRIMEB cavity. The solvation dynamics of 4-AP within the TRIMEB cavity is 250 ± 50 ps which is substantially slower than that observed in bulk water. The dramatic retardation of the solvation dynamics inside TRIMEB cavity is attributed to the restriction imposed on the motion of the water molecules entrapped inside the TRIMEB nanocavity and to the dynamic exchange of bound and free water molecules.

Acknowledgements

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