Excitation Wavelength Dependence of Solvation Dynamics in a Water Pool of a Reversed Micelle

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We have investigated the excitation wavelength dependence of solvation dynamics in the water pool of a reversed micelle using dynamic Stokes shift method. The solvation dynamics displays nanosecond and subnanosecond components, which are almost independent of the excitation wavelength. On the other hand, the total dynamics Stoke shift decreases with increasing the excitation wavelength.

Dynamics of a liquid in a restricted environment often differs markedly from that in a bulk solution.[1,2] Especially, effect of confinement of water is a key issue to understand solvent effects on many biological processes. A water pool (WP) in a reversed micelle (RM), a surfactant-coated water droplet in a water-in-oil microemulsion, is an elegant model of water molecules in confined environments. The size of the RM is nearly proportional to the water content, which is often expressed as the molar ratio of water to the surfactant, $w_0 = [\text{water}]/[\text{surfactant}]$. Various time-resolved spectroscopic studies have been performed in RMs to reveal confinement and interfacial effects on dynamics of liquids and solvated species.[1–7] Recently dynamic fluorescence Stokes shift experiments were performed in a WP of RMs to study solvation dynamics in a confinement system.[1–5] In bulk water the solvation dynamics completes within a few picoseconds.[8] For the solvation dynamics in RMs, a striking finding is that the time scale of the dynamics ranges over four orders of magnitude from a subpicosecond to several nanoseconds.[1–5]

In this letter, we report on the excitation wavelength dependence of the solvation dynamics in RM. Time-resolved fluorescence measurements were performed on a water/Aerosol-OT (AOT)/isooctane microemulsion with an ionic probe of coumarin 343 (C343). We find that the fluorescence spectrum of the probe molecule in the RM shows significant excitation wavelength dependence, reflecting heterogeneity of microscopic environment in the RM. Such wavelength-selective fluorescence measurements have been used to study micro-heterogeneous environments such as lipid vesicles, very viscous solutions and confined systems.[9] We show that the excitation wavelength dependence of the fluorescence dynamic Stokes shift provides information on the location dependence of the solvation dynamics in the RM.

The excitation laser is a femtosecond Ti:sapphire oscillator (Spectra-Physics, Maitai), which is tunable from 780 to 920 nm. The repetition rate is reduced by a pulse-picker (Spectra-Physics) down to 8 MHz, and the second harmonic is generated in a BBO crystal. The fluorescence is collected and detected by a photomultiplier tube after passing through a monochromator. A signal was processed by a time-correlated single photon counting system (Becker & Hickel Gmbh, SPC-630). FWHM of the response function is about 250 ps. C343, AOT, and isooctane were purchased from Exciton, Sigma, and Wako Pure Chemicals, respectively, and used without further purification. Water was obtained from a Millipore Milli-Q purification system. Steady-state absorption and fluorescence spectra were recorded by Shimadzu UV-3150 and RF-5300PC, respectively. The diameter of the reversed micelle was measured by a dynamic light scattering technique (DLS-7000, Photal). All the measurements were done at 20 C.

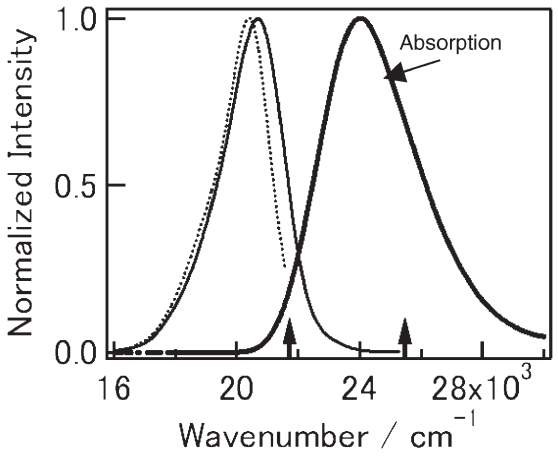

Figure 1. Absorption spectrum and fluorescence spectra observed by excitation at 460 nm (dotted) and 390 nm (solid line) of C343 in a reversed micelle. The arrows indicate the excitation wavelengths.

Figure 1 shows the absorption and fluorescence spectra of C343 in a water/AOT/isooctane microemulsion with w_0 of 30. The size of micelle is measured to be 17.4 ± 2.7 nm for the present system. Considering the length of the AOT molecule (1.2 nm), the diameter of the WP is estimated to be about 15 nm. The absorption spectrum of the RM is blue-shifted compared to that in bulk water by about 10 nm. The fluorescence spectrum shows a significant excitation wavelength (λ_{ex}) dependence. In bulk water, the peak wavelength and FWHM of the spectrum are 486.1 nm and 2023 cm^{-1}, respectively, with no excitation wavelength dependence of the fluorescence spectrum. In the RM, the peak wavelength is located at 481.9 nm and the FWHM is 2333 cm^{-1} when $\lambda_{ex} = 390$ nm. With decreasing the excitation energy, the fluorescence spectrum becomes red-shifted accompanying spectral narrowing. At $\lambda_{ex} = 460$ nm, the peak wavelength is 489.2 nm, and the FWHM is 1971 cm^{-1}. This in-

dicates that there is an inhomogeneous distribution of the microscopic environment in the RM. RMs with smaller w_0 values show a more blue-shifted absorption spectrum,[3,4,10] and the excitation wavelength dependence is more prominent.[10] Therefore, a spectral component with a higher energy results from a probe molecule located in the vicinity of the surfactant. Qualitatively, this is reasonable since the effective dielectric constant around the head-group is considered to be lower than that in the bulk.

Figure 2 shows time-resolved fluorescence spectra of C343 in the RM with w_0 of 30. The fluorescence lifetime in the bulk water is 4.3 ns. The fluorescence decay was measured at more than twenty different wavelengths, and time-resolved spectra were reconstructed in terms of the steady-state fluorescence spectrum by the ordinary procedure. It can be observed that the dynamic Stokes shift takes place in a nanosecond time scale. The solvent response function $C(t)$, which characterizes the solvation dynamics, is defined as $C(t) = (\nu(t) - \nu(0))/(\nu(\infty) - \nu(0))$, where $\nu(t)$ is the peak wavelength of the fluorescence spectrum at t. The solvent response function $C(t)$ is reproduced well by a bi-exponential function ($C(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)$) with time constants of subnanosecond and a few nanoseconds.

The parameters of $C(t)$ obtained with different excitation wavelengths are summarized in Table 1 together with the total dynamic Stokes shift $C(t)$, which is defined as $\Delta\nu = \nu(\infty) - \nu(0)$. Table 1 shows several important aspects of microscopic environment in the RM. First, the time scale of $C(t)$ does not depend on the excitation wavelength; at any λ_{ex}, $C(t)$ shows a bimodal feature with subnanosecond and a few nanosecond time constants, and the time constants and pre-exponential factors (a_1 and a_2) are independent of λ_{ex} within an experimental error. This suggests that both the subnanosecond and a few nanosecond dynamics originate from a probe molecule located in an identical microscopic environment. Secondly, the total shift $\Delta\nu$ drastically decreases when λ_{ex} increases. In the bulk water $\Delta\nu$ was reported to be 1481 cm^{-1}, which was measured by a femtosecond fluorescence up-conversion technique.[8] This indicates that there is a component of solvation dynamics whose time scale is faster than our time resolution ($\approx$100 ps), and hence, is missed in our study. The amount of the missing component depends on λ_{ex}.

Table 1. Parameters of the solvent response function $C(t)$ and the total dynamic Stokes shift $\Delta\nu$

λ_{ex}/nm	$\Delta\nu$/cm^{-1}	a_1	τ_1/ns	a_2	τ_2/ns
390	707	0.77	0.22	0.23	2.02
425	422	0.71	0.31	0.29	2.46
440	363	0.64	0.24	0.36	1.70
460	225	0.63	0.27	0.37	1.75

The λ_{ex} dependence of $C(t)$ and $\Delta\nu$ can be qualitatively rationalized in terms of a two-state model where it is assumed that there are two different microscopic regions in the WP; one is a bulk-like region (core of WP) where the solvation dynamics takes place much faster than our time-resolution, and the other is a region in the vicinity of the surfactant head-group where the dynamics is slower. The subnanosecond and nanosecond components result from the probes in the surface region. Excitation at the red side of the absorption spectrum preferentially selects the probes in the bulk-like region. The subpicosecond dynamic Stokes shift due to these molecules is not detected in our set up. Studies on dependence of $C(t)$ on both the micelle size and excitation wavelength are now under investigation. Study of λ_{ex} dependence of solvation dynamics using femtosecond time resolution may reveal the contributions of bulk-like and surface region.

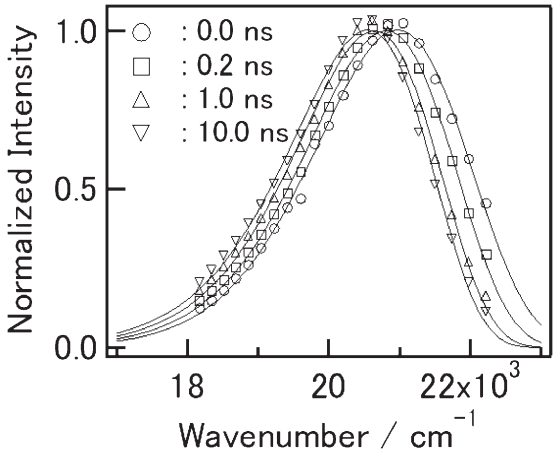

Figure 2. Time-resolved fluorescence spectra of C343 in a reversed micelle. The solid lines are the reconstructed spectra.

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