The Ultrafast Relaxation Dynamics of a Viscosity Probe Molecule in an AOT-Reversed Micelle: Contribution of the Specific Interactions with the Local Environment

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The ultrafast relaxation dynamics of a widely used viscosity probe molecule, auramine O (AuO), was investigated in water and a water/aerosol−OT (AOT)/*n*−heptane reversed micelle. We discussed the contribution of specific interactions between AuO and the local environment to the relaxation dynamics. The transient absorption spectra of AuO showed that the nonradiative relaxation process of the photoexcited AuO in the AOT-reversed micelle was approximately 1 order slower than that in bulk water and the relaxation rate decreased with a decrease of the size of the reversed micelle. The slowing down of the relaxation was attributed to a depletion of the ultrafast solvation dynamics of water molecules in the interfacial area of the reversed micelle as well as an increase of viscosity, which strongly suggested that the viscosity of the reversed micelle determined from the fluorescence yield of AuO was somewhat overestimated. In addition, it was observed that the absorption coefficient of the twisted intramolecular charge transfer-like (TICT-like) intermediate state of the AuO in the reversed micelle was about half as large as that in bulk water. A decrease of the refractive index of the TICT-like state was also observed in the reversed micelle by the ultrafast transient lens measurements. The reduction of both the absorption coefficient and the refractive index of the TICT-like state indicated a considerable change of the molecular structure or the charge distribution of the TICT-like state. Such a change of the TICT-like state suggested the existence of strong interactions between AuO and AOT. These interactions would also affect the relaxation dynamics and the fluorescence yield of the AuO in the reversed micelle.

Introduction

It is well-known that the structure, dynamics, and physicochemical properties of water molecules confined in a nanometer-sized space are greatly different from those of bulk water.[1] Water/aerosol−OT (AOT)/oil reversed micelle is one such nanometer-sized confined water system and has been extensively studied as a model for water molecules on proteins or biological membranes to understand the chemical and biological processes in such systems.[2−11] These studies have shown that an AOT reversed micelle is spherical, and the radius of water droplet r is proportional to the water−surfactant molar ratio w_0.

$$w_0 = \frac{[H_2O]}{[AOT]} \tag{1}$$

$$r = 0.2w_0[nm] \tag{2}$$

The structure of the AOT reversed micelle was investigated by NMR,[12−17] IR,[17−19] and Raman spectroscopy.[20] The solvation dynamics and the dielectric relaxation process of water inside the reversed micelle were also studied by time-resolved fluorescence dynamic Stokes shift[21−24] and THz time-domain spectroscopy,[25−27] respectively. These studies have shown that the water molecules inside the reversed micelle are roughly classified into two types. In the interfacial area of the reversed micelle (water/AOT interface) the water molecules are immobilized due to strong hydration with AOT molecules, and are called "bound water". On the other hand, there are bulklike water molecules in the center area of the reversed micelle. The number of the bulklike water molecules increases with an increase of the size of the reversed micelle.

The physicochemical properties of water in the reversed micelle, such as viscosity or polarity, have also attracted a lot of interest.[28−30] This is because such properties strongly affect the molecular dynamics inside the reversed micelle, including rotational and translational relaxation, change of conformation, isomerization, electron transfer, and so on. In general, the physicochemical properties were studied by using a fluorescence probe molecule of which fluorescence yield, lifetime, or peak position sensitively reflects the local environment around the probe molecule. However, it should be noted that in an AOT reversed micelle, especially in its interfacial area, the relaxation dynamics of the fluorescence probe molecule would be greatly different from that in bulk solution due to specific interactions with the interface (e.g., charge-transfer complex formation with AOT molecules[31]). Hence, to evaluate the physicochemical properties of the interfacial area of the reversed micelle, it is necessary to investigate not only the static character of the spectra, but also the relaxation dynamics of the probe molecule itself.

Auramine O (AuO: Figure 1) is a widely used viscosity probe molecule. The fluorescence emission process of photoexcited AuO competes with the internal conversion process to a

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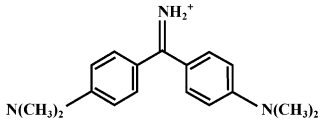


Figure 1. Chemical structure of AuO.

nonradiative intermediate state via intramolecular twisting motion of the phenyl groups. In viscous media, the twisting motion is prevented and the fluorescence yield (φ_f) of AuO increases.[32,33] Therefore, provided *the nonradiative decay process is dominantly affected by solvent viscosity and insensitive to other factors*, the viscosity around the AuO molecules can be estimated by measuring φ_f. Previously, an attempt was made to estimate the viscosity of the interfacial area of the reversed micelle from the φ_f of AuO;[28] AuO is preferentially located in the interfacial area due to electrostatic interaction, because AuO is a cationic dye and AOT is an anionic surfactant. However, the above premise has not been experimentally confirmed yet. In addition, even the relaxation dynamics of AuO in bulk water have not been fully explained, because the AuO in bulk water decays extremely fast ($\sim$1 ps) and it is difficult to measure the dynamics with sufficient time resolution.

In this study, we discussed the influence of specific interactions with the local environment on the relaxation dynamics of a fluorescent probe molecule. The relaxation dynamics of AuO following the $S_1 \leftarrow S_0$ excitation was investigated both in bulk water and in a water/AOT/*n*-heptane reversed micelle by using transient absorption spectroscopy and the ultrafast transient lens (UTL) method: The UTL method is a technique to measure the refractive index change of the solution with subpicosecond time resolution,[34−43] which reflects a change of electronic state or structure of the molecules in a nanometer-sized space due to interactions with the local environment.[37,38] It was revealed by the transient absorption measurements that the nonradiative relaxation process of the photoexcited AuO was affected by ultrafast solvation dynamics as well as viscosity of the local environment. The contribution of the solvation dynamics to the relaxation dynamics strongly suggested that the viscosity of the AOT reversed micelle determined from φ_f of the AuO was somewhat overestimated. In addition, the transient absorption spectra and the UTL signals showed that the molecular structure or charge distribution of the nonradiative intermediate state was considerably different from those in bulk water due to strong interactions between AuO and AOT. We considered that these interactions would also affect φ_f of the AuO.

Experimental Section

AuO was obtained from Wako Chemicals and purified once by recrystalization from warm NaCl solution.[44] AOT (Wako Chemicals) and *n*-heptane (Kanto Kagaku) were used as purchased. AOT was dissolved in *n*-heptane with a concentration of 0.8 M as a stock solution. The sample solutions were prepared by adding a constant amount of water and a known amount of the AOT/*n*-heptane stock solution to *n*-heptane. The water−surfactant molar ratio of the sample solution, w_0, was controlled by adjusting the amount of the stock solution. The sample solutions were thoroughly shaken and sonicated for 10 min to ensure the formation of a reversed micelle. The concentrations of water and AuO were kept constant at 2.0 M and 0.3 mM, respectively. The radius of the reversed micelle was calculated from eq 2.

For the transient absorption measurement, a Ti:Sapphire oscillator (Coherent, MIRA BASIC) with a regenerative-amplifier (Clark, CPA-1000) was used as a light source. The output beam (800 nm, 200 fs fwhm, 1 kHz repetition) was split into two beams. The main part of the beam was frequency-doubled by a BBO crystal and used as a pump beam (400 nm). The other part of the beam was passed through an optical delay line and focused into a 1-cm D_2O cell to generate a white-light continuum, which was used as a probe beam. A small part of the probe beam was used as a reference. The pump and probe beams were crossed at a small angle and focused on the sample cell. The intensities of the probe beam and the reference beam were measured by a multichannel CCD spectrometer (Hamamatsu, PMA-11), and the absorbance change of the sample solutions was calculated with a personal computer. The spectral data were corrected for the dispersion of the probe pulse at the sample by using the measured dispersion from two-photon absorption of glass filters. The response function of the whole system was determined from the width of the two-photon absorption peak of the glass filters; it was about 300 fs fwhm. In the measurement of the sample solutions, the power of the pump beam was less than 200 μJ/pulse and it was confirmed that no nonlinear process such as multiphoton absorption was taking place.

The principle and the experimental setup for the UTL measurement have been described in detail elsewhere.[36] Only a brief outline is given here. The UTL method is a kind of pump−probe experiment. The pump pulse having a Gaussian-type spatial distribution of the intensity generate a lens-like spatial distribution of the refractive index (termed "transient lens") temporary in the sample solution through interactions with the sample solution. The transient lens focuses or defocuses the probe pulse incident to this region after passing through an optical delay line. Then, the refractive index change was measured as a change of the intensity of the center area of the probe pulse through a pinhole. In our experiments, a Ti:Sapphire oscillator (Coherent, MIRA 900F; centered at 800 nm, 76 MHz repetition) was used as the light source. The laser output was split into two beams. One beam was used as a pump beam after frequency doubling by a BBO crystal. The intensity of the pump beam was modulated at 1.1 MHz with an acousto-optic modulator. The other beam was used as a probe beam after passing through an optical delay line. The pump and probe beams were set collinear with a dichroic mirror and focused on the sample cell. The refractive index change of the sample was detected as a change of the intensity of the center area of the probe beam by a small-area ($\phi = 0.1$ mm) avalanche photodiode. The output of the photodiode passed through a preamplifier and a homemade passive band-pass filter before being sent to a lock-in amplifier. The power of the pump beam was less than 200 pJ/pulse. The response function of the whole system was about 400 fs fwhm. In both transient absorption and the UTL measurements, the relative polarization between the pump beam and the probe beam was set parallel. The sample solutions were circulated through a quartz flow cell (0.5-mm path length) to avoid degradation. Static absorption spectra were measured by a UV−vis spectrometer (JASCO, V-570). All measurements were performed at 296 K.

Results

Absorption Spectra of AuO. The absorption spectra of AuO have two peaks of $S_2 \leftarrow S_0$ and $S_1 \leftarrow S_0$.[32] The spectra in bulk water obeyed Beer's law in the concentration range from 3×10^{-6} M to 4×10^{-4} M, and we confirmed that AuO did not form dimer or another aggregated state under our experimental conditions. The absorption spectra of AuO in the AOT reversed micelle indicated a slight blue shift of both the S_1 and the S_2 peaks. The blue shift of the spectra increased with decrease of

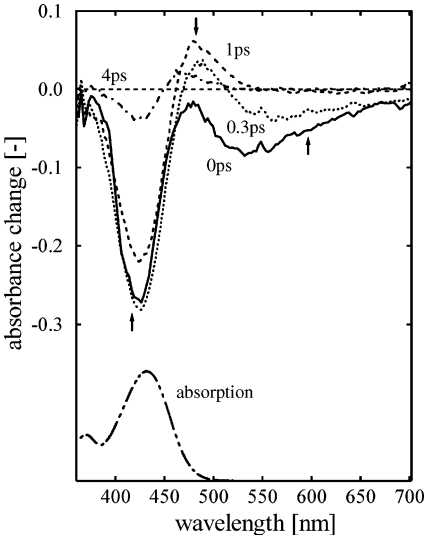


Figure 2. The transient absorption spectra of AuO in bulk water at 0 ps (solid line), 0.3 ps (dotted line), 1 ps (broken line), and 4ps (dash−dotted line) after excitation. The dash−double dotted line is the absorption spectrum of AuO in bulk water.

w_0, and a decrease of the S_1 peak and an increase of the S_2 peak were concomitantly observed. The blue shift of the spectra indicated that the microenvironment around the AuO molecule was different from that in bulk water and it was attributed to an incompleteness of hydration of the AuO molecule.[28]

Transient Absorption Spectra of AuO in Bulk Water. Figure 2 shows the transient absorption spectra of AuO in bulk water following the $S_1 \leftarrow S_0$ excitation. Just after the excitation, a decrease of the absorbance was observed, which was composed of a bleaching band of the ground state at 380−475 nm and a broad gain band of the fluorescent excited state at 475−700 nm. The gain band decayed within 1 ps, accompanied by the rise of a transient absorption band of the nonradiative intermediate state at ∼480 nm. The decay of the transient absorption band and the recovery of the bleaching band proceeded simultaneously within several picoseconds. The time evolutions of the absorbance at several wavelengths (3 arrows in Figure 2) are shown in Figure 3. The time evolutions of the gain band and the transient absorption band were fitted well by the sum of exponential functions convoluted with the response function of the apparatus (Table 1). The lifetime of the gain band (τ_1 at 551 and 600 nm) was ∼0.3 ps and it was the same as the rise time of the transient absorption band (τ_1 at 482 and 502 nm). Since the lifetimes of the gain band were almost independent of wavelength, the red shift of the gain band was due to an overlap with the transient absorption band. The bleaching band was nearly constant during ∼0.3 ps after excitation, followed by the recovery process, which consisted of two exponential decay components: the main part (∼95%) decayed with a time constant of 1.4 ps (τ_2) and the residual decayed with a time constant of ∼15 ps (τ_3). These time constants of the recovery of the bleaching band corresponded well to those of the decay of the transient absorption band.

Transient Absorption Spectra of AuO in AOT Reversed Micelle. Figure 4 shows the transient absorption spectra of photoexcited AuO in a water/AOT/ *n*-heptane reversed micelle (r = 2 nm). The transient absorption spectra in the reversed micelle as well as those in bulk water were composed of three components; the gain band of the fluorescent excited state, the transient absorption band of the nonradiative intermediate state, and the bleaching band of the ground state. On the other hand, there were two apparent differences between the transient absorption spectra in the reversed micelle and those in bulk water. First, the time evolutions of the spectra in the reversed micelle were much slower than those in bulk water, and the time constants increased with a decrease of the size of the

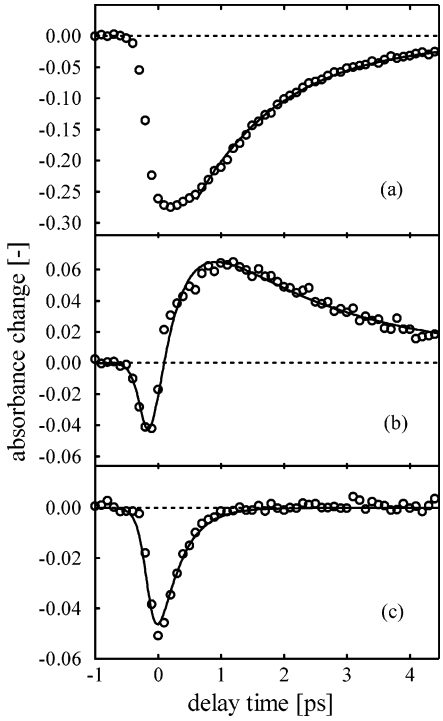


Figure 3. The time evolutions of the absorbance change of photoexcited AuO in bulk water at (a) 421 nm, (b) 482 nm, and (c) 600 nm. The solid lines are results of the least-squares fitting. The fitting for 421 nm was done without the data in delay time < 0.6 ps where the absorbance was almost constant.

TABLE 1: Kinetic Parameters Determined by a Least-Square Fitting of the Transient Absorption Spectra of AuO in Bulk Water[a]

wavelength [nm]	A_1 [ps][b]	τ_1 [ps][c]	A_2 [-][d]	τ_2 [ps][e]	A_3 [-][f]	τ_3 [ps][g]
421			−0.43	1.4	−0.011	23
482	−0.26	0.38	0.12	2.0	0.009	15
502	−0.27	0.30	0.09	1.6	0.003	20
551	−0.15	0.28			0.004	16
600	−0.09	0.35				

[a] The model function is $\int_{-\infty}^{t} f(t-s)R(s)ds$, $f(t) = A_0 + \sum_{i=1}^{3} A_i \exp(-t/\tau_i)$, and $R(t)$ is the response function of the apparatus. [b] ±0.01. [c] ±0.1 ps. [d] ±0.01. [e] ±0.2 ps. [f] ±0.001. [g] ±5 ps.

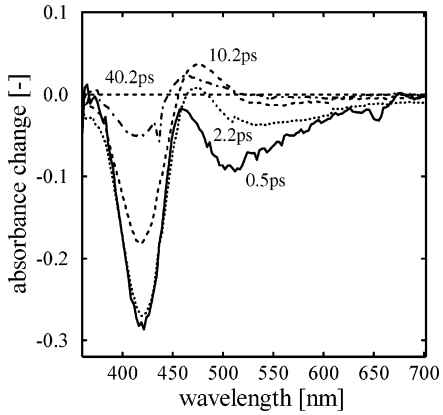


Figure 4. The transient absorption spectra of AuO in the AOT/water/ *n*-heptane reversed micelle at 0.5 ps (solid line), 2.2 ps (dotted line), 10.2 ps (broken line), and 40.2 ps (dash−dotted line) after excitation. The radius of the reversed micelle was 2 nm (w_0 = 10).

TABLE 2: Decay Time Constants of the Gain Band (τ_1) and the Recovery Time Constants of the Bleaching Band (τ_2) in the Reversed Micelle and in Bulk Water[a]

radius of the reversed micelle [nm]	τ_1 [ps]	τ_2 [ps]
0.8	8.0 ± 0.1	30.0 ± 1.0
1.4	5.4 ± 0.2	20.2 ± 1.5
2.0	3.7 ± 0.1	15.4 ± 0.5
4.0	2.3 ± 0.1	12.3 ± 0.5
8.0	1.9 ± 0.1	10.4 ± 0.5
bulk water	0.28 ± 0.1	1.4 ± 0.2

[a] τ_1 and τ_2 were determined by a least-squares fitting of the time evolution of the transient absorption spectra at 551 nm and at 421 nm, respectively.

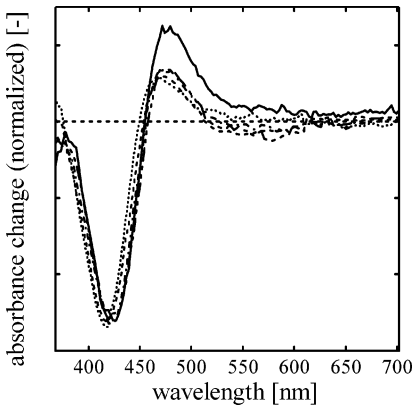


Figure 5. The normalized transient absorption spectra of AuO in bulk water (solid line) and that in the AOT reversed micelle (dotted line: $r = 0.8$ nm, broken line: $r = 2$ nm, dash−dotted line: $r = 4$ nm, dash-double dotted line: $r = 8$ nm). To exclude the overlap of gain band on the transient absorption band, all spectra were normalized at the delay time when the bleaching band recovered to 50% (the gain band had completely decayed at that time).

reversed micelle (Table 2). Second, the absorption coefficient of the transient absorption band was apparently smaller in the reversed micelle compared with the value in bulk water. The intensity-normalized transient absorption spectra (Figure 5) showed that the absorption coefficient of the transient absorption band (~480 nm) in the reversed micelle were about half as large as those in bulk water. It should be noted that the absorption coefficient of the transient absorption band was independent of the micellar size, while the relaxation rate strongly depended on it.

UTL Signals of AuO in Bulk Water and the AOT Reversed Micelle. Figure 6 shows UTL signals of the photoexcited AuO in bulk water and reversed micelle solution ($r = 2$ nm). A temporal decrease of the refractive index was observed both in bulk water and in the reversed micelle solutions. In bulk water, the UTL signal was fitted well by an exponential function convoluted with the response function of the apparatus (Figure 6a). The time constant of the refractive index change was 0.21 ps. On the other hand, in the reversed micelle solutions, the refractive index change could not be fitted by an exponential function: It was composed of the sum of two exponential functions (Figure 6b). The time constants of the UTL signals were shown in Figure 7.

Discussion

Influence of the Solvation Dynamics on the Nonradiative Relaxation Process of AuO. First, we discuss the influence of specific interactions between AuO and solvent molecules on the nonradiative relaxation process of AuO that determines the φ_f. The transient absorption spectra of AuO in bulk water

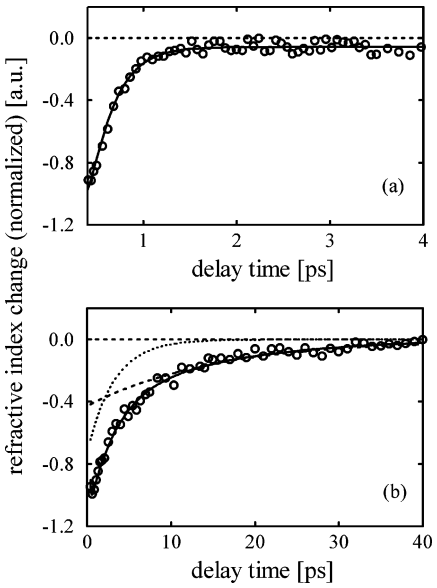


Figure 6. The refractive index change of the photoexcited AuO (a) in bulk water and (b) in the AOT reversed micelle ($r = 2$ nm). The solid line in (a) is a result of the least-squares fitting with an exponential function. The solid line in (b) is a result of the least-squares fitting with the sum of two exponential functions. The dotted line and broken line in (b) are the contribution of the fast and slow decay components, respectively. The signal in the delay time < 0.36 ps was excluded, because the refractive index change due to the optical Kerr effect of the cell and solvent overlapped as an artifact in that region.

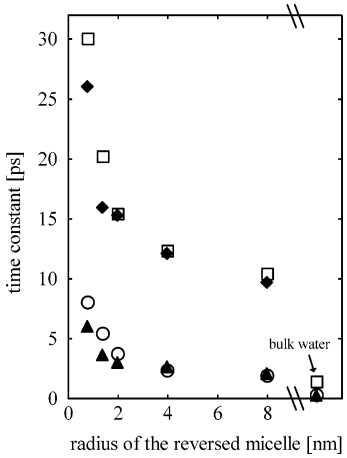
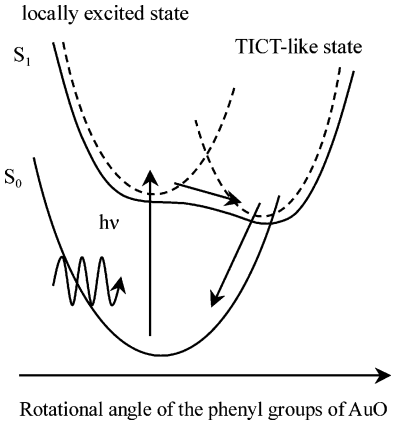


Figure 7. Time constants of the refractive index change of the photoexcited AuO in bulk water and the reversed micelle (filled triangles: fast component, filled rhombs: slow component). The lifetimes of the locally excited state (open circles) and the TICT-like state (open squares) of AuO were also plotted.

showed qualitatively good agreement with the model proposed for the relaxation process of photoexcited AuO in alcohol solutions (Scheme 1).[45−48] Photoexcited AuO relaxed from the fluorescent locally excited state to the adiabatically coupled nonradiative twisted intramolecular charge transfer-like (TICT-like) intermediate state via a diffusive twisting motion of the phenyl groups of AuO. This process was observed as the decay of the gain band and the rise of the transient absorption band (τ_1 component in Table 1), because these bands originated from the stimulated emission from the locally excited state and the absorption of the TICT-like state, respectively. Following the relaxation process of the locally excited state to the TICT-like state, an internal conversion process from the TICT-like state to the ground state proceeded with the decay of the transient

SCHEME 1: Relaxation Process of Photoexcited AuO



absorption band and the recovery of the bleaching band of the transient absorption spectra (τ_2 component in Table 1). Finally, the vibrational relaxation process of the ground state was observed as a weak long-lived component (τ_3 component in Table 1). There was no direct relaxation path from the locally excited fluorescent state to the ground state, which corresponded well to the absence of a fast component in the recovery process of the bleaching band.

Although the transient absorption spectra in bulk water qualitatively agreed well with the above model, the time evolution of the relaxation process in bulk water was apparently different from that in alcohol. In bulk water, the lifetimes of the locally excited fluorescent state and the nonradiative TICT-like state were ~0.3 ps and ~1.5 ps, respectively (Table 1), while they were ~3 ps and ~30 ps in ethanol.[45,46] As mentioned in the above section, solvent viscosity strongly affects the relaxation dynamics of the photoexcited AuO. In this case, however, the viscosity of water was almost the same as that of ethanol (~1.0 cP), and therefore the difference between the decay rates of AuO in water and those in ethanol originated not from solvent viscosity, but from the specific interactions between AuO and solvent molecules. Here, we consider the contribution of ultrafast solvation dynamics of solvent molecules to the relaxation process of AuO. The relaxation process of AuO from the locally excited state to the TICT-like state proceeds via twisting motion of phenyl groups with intramolecular charge transfer. In a solution, the rate of a reaction including a charge transfer process was strongly dependent on the rate of a solvation process as well as that of the charge-transfer process.[49] Especially, in the case that the time scale of the charge transfer process is comparable or faster than that of the solvation process, these processes proceed cooperatively and the reaction rate increases with an increase of the rate of the solvation. In a low viscosity solvent such as water or ethanol, the time scale of the charge transfer of AuO is comparable to that of the solvation (subpicosecond in bulk water). Therefore, in these solvents the faster solvation dynamics accelerated the relaxation process from the locally excited state to the TICT-like state. This model corresponded well to our experimental results, because the solvation dynamics of water[50] are much faster than those of ethanol.[51] As for the internal conversion process from the TICT-like state to the ground state, we considered that the larger energy stabilization of the TICT-like state by the solvation process induced a decrease of the potential energy gap between these states, which increased the internal conversion rate. Thus, we concluded that the ultrafast solvation dynamics of the solvent molecules contributed to the nonradiative relaxation process of AuO, which affected φ_f of AuO.

Taking the contribution of the ultrafast solvation dynamics into account, we next discuss the viscosity in the interfacial area of the reversed micelle. Previously, the viscosity in the interfacial area of the AOT reversed micelle was estimated by comparing φ_f of AuO in the reversed micelle with φ_f in glycerol-water mixtures. It was reported that the local viscosity in the interfacial area of the reversed micelle was more than 10 times larger than the viscosity of bulk water and increased with the decrease of micellar size.[28] This behavior of the local viscosity in the reversed micelle corresponded well to the relaxation dynamics of the photoexcited AuO observed in our experiments (Table 2). However, the static absorption spectra of AuO in the reversed micelle indicated that hydration of the AuO was incomplete in the reversed micelle, which suggested a decrease of energy stabilization by solvation dynamics of nearby water molecules. In addition, it was reported that the solvation of water molecules (100 fs−1 ps time scale in bulk water) was remarkably slowed in the reversed micelle (100−1000 ps time scale) based on time-resolved fluorescence dynamic Stokes shift measurements;[21−24] specific interaction with surfactant headgroup and the restricted environment itself were considered to play an important role in limiting the mobility of water. Therefore, we consider that the depletion of the solvation dynamics by water molecules in the interfacial area of the reversed micelle as well as the increase of the viscosity slowed the nonradiative relaxation process of the AuO, which induced the increase of φ_f of AuO. In other words, there was a strong probability that the local viscosity determined from φ_f of AuO was somewhat overestimated, although it was difficult to estimate the contribution of the solvation dynamics quantitatively from the following reasons. First, the specific interactions between AuO and AOT would also contribute to the relaxation process (discussed in the next section). Second, the relaxation rate determined in our experiments, especially the lifetime of the TICT-like state, would be affected by rotational motion of the AuO molecule (of the order of tens of picoseconds) because the relative polarization between pump and probe pulses was set parallel in our experiments.

The relaxation process of AuO in the reversed micelle did not show a superposition of the bulk and bound water properties. This is because the bulk water phase and the bound water phase were not completely separated in the reversed micelle and AuO interacted with the water molecules in both phases due to its relatively large size (~1 nm); the thickness of the bound water was subnanometer scale.[19]

Influence of the Interactions with the Micellar Interface on the Nonradiative Relaxation Dynamics of AuO. In the transient absorption spectra of AuO in the reversed micelle, a reduction of the absorption coefficient of the TICT-like intermediate state was observed in addition to the increase of the lifetimes of both the locally excited state and the TICT-like state (Figure 5). Since the absorption coefficient of a dye molecule is generally independent of solvent viscosity, the reduction of the absorption coefficient indicated the influence of factors other than viscosity on the relaxation dynamics of the photoexcited AuO in the reversed micelle. We considered that the decrease of the absorption coefficient of the TICT-like state originated from the specific interactions between AuO and AOT. This is because (1) AuO was located at the interface of the reversed micelle and (2) the absorption coefficient was almost independent of the size of the reversed micelle (Figure 5), while the influence of the interactions with water and the restricted environment generally depend on the micellar size. The contribution of the interactions with bound water should also

depend on the micellar size, since the thickness of the bound water is comparable to the size of the AuO molecule and it increases with an increase of the micellar size.[19] Steric hindrance of the intramolecular twisting motion due to the AOT interface or electrostatic interaction with the polar headgroup of AOT molecules were probable candidates to explain the reduction of the absorption coefficient. These interactions affected the molecular structure (e.g., twisting angle of phenyl groups) or charge distribution of the TICT-like state, which should induce a considerable change in the absorption coefficient. Changes in molecular structure and/or charge distribution of the TICT-like state were also indicated by the results of the UTL measurements. It has been reported that the changes in molecular structure and/or charge distribution result in a change of the refractive index.[34−43] In bulk water, the refractive index change of AuO following $S_1 \leftarrow S_0$ excitation was fitted by an exponential function (Figure 6a), and the time constant (0.21 ps) agreed well with the lifetime of the locally excited state (0.28 ps). On the other hand, in the reversed micelle solution, the decrease of the refractive index was composed of the sum of two exponential functions (Figure 6b), of which time constants corresponded well to the lifetimes of the locally excited state and the TICT-like state (Figure 7). This result means that the refractive index of the TICT-like state was smaller than that of the ground state in the reversed micelle, while they were almost the same in bulk water. Therefore, we concluded that the reduction of the absorption coefficient and the refractive index was induced by the changes in molecular structure and/or charge distribution of the TICT-like state due to steric hindrance of the intramolecular twisting motion or electrostatic interaction with the polar headgroup of AOT. We suggested that these interactions between the AuO and AOT interface also contributed to the characteristic relaxation and the change of φ_f of AuO in the reversed micelle.

Summary

The relaxation dynamics of photoexcited AuO in water and water/AOT/ *n*-heptane reversed micelle was investigated by using transient absorption spectroscopy to clear the influence of the factors other than solvent viscosity on the relaxation dynamics. The transient absorption spectra of AuO in the reversed micelle showed that the relaxation dynamics of the photoexcited AuO in AOT reversed micelle was about one order slower than that in bulk water. In the past studies in which φ_f of AuO was investigated, the decrease of the relaxation rate has been attributed to an increase of the viscosity inside the reversed micelle. On the other hand, the transient absorption spectra in bulk water shown that the relaxation process of the photoexcited AuO from the emissive locally excited state to the nonradiative TICT-like intermediate state was much faster than that in ethanol. Since the viscosity of water is nearly equal to that of ethanol, we considered that the relaxation dynamics of AuO was affected not only by solvent viscosity, but also by ultrafast solvation dynamics accompanying with the relaxation process. Therefore, the slower relaxation dynamics in the reversed micelle was attributed to a depletion of the ultrafast solvation dynamics of water molecules as well as an increase of viscosity in the interfacial area of the reversed micelle. These results strongly suggested that the local viscosity inside the reversed micelle determined from φ_f of AuO was somewhat overestimated. In addition, we observed a decrease of the absorption coefficient and the refractive index of the TICT-like intermediate state in the reversed micelle. These changes in the absorption coefficient and the refractive index indicated a considerable change of molecular structure or charge distribution of the TICT-like state due to steric hindrance of the intramolecular twisting motion and/or electrostatic interaction with the polar headgroup of AOT. These interactions would also induce a characteristic relaxation and the change of φ_f of AuO in the reversed micelle.

Our experimental results provide one example showing the importance of separating the contribution of the physicochemical properties to the dynamics of a solute molecule from that of the specific interactions with the local environment in inhomogeneous systems of nanometer scale such as AOT reversed micelle. To understand the molecular dynamics in such systems quantitatively (not merely qualitatively), investigating the interactions between the probe molecule and local environment in ultrafast time scale is indispensable as well as studying the static spectroscopic properties of the molecule.

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References and Notes

(1) Bhattacharyya, K.; Bagchi, B. *J. Phys. Chem. A* **2000**, *104*, 10603.
(2) Day, R. A.; Robinson, B. H. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 132.
(3) Zulauf, M.; Eicke, H. F. *J. Phys. Chem.* **1979**, *83*, 480.
(4) Sein, E.; Lalanne, J. R.; Buchert, J.; Kielich, S. J. *J. Colloid Interface Sci.* **1979**, *72*, 363.
(5) Gulari, E.; Bedwell, B. *J. Colloid Interface Sci.* **1980**, *77*, 202.
(6) Cacazabat, A. M.; Langevin, D. *J. Chem. Phys.* **1981**, *74*, 3148.
(7) Clarke, J. H. R.; Nicholson, J. D.; Regan, K. N. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 1173.
(8) Assih, T.; Larche, F.; Delord, P. *J. Colloid Interface Sci.* **1982**, *89*, 35.
(9) Kotlarchyk, M.; Huang, J. S.; Chen, S. H. *J. Phys. Chem.* **1985**, *89*, 4382.
(10) Hirai, M.; Hirai, R. K.; Sanada, M.; Iwase, H.; Mitsuya, S. *J. Phys. Chem. B* **1999**, *103*, 9658.
(11) Luisi, P. L.; Straub, B. E. *Reverse Micelles: Biological and Technological Relevance of Amphiphilic Structures in Apolar Media*; Plenum: New York, 1984.
(12) Wong, M.; Thomas, J. K.; Nowak, T. *J. Am. Chem. Soc.* **1977**, *99*, 4730.
(13) Eicke, H. F.; Zinsli, P. E. *J. Colloid Interface Sci.* **1978**, *65*, 131.
(14) Maitra, A. N.; Eicke, H. F. *J. Phys. Chem.* **1981**, *85*, 2687.
(15) Heatley, F. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 517.
(16) Hauser, H.; Haering, G.; Pande, A.; Luisi, P. L. *J. Phys. Chem.* **1989**, *93*, 7869.
(17) Kawai, T.; Hamada, K.; Shindo, N.; Kon-no, K. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2715.
(18) Sunamoto, J.; Hamada, T.; Seto, T.; Yamamoto, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 583.
(19) Zhou, G. W.; Li, G. Z.; Chen, W. J. *Langmuir* **2002**, *18*, 4566.
(20) D′Aprano, A.; Lizzio, A.; Liveri, V. T.; Aliotta, F.; Vasi, C.; Migliardo, P. *J. Phys. Chem.* **1988**, *92*, 4436.
(21) Bhattacharyya, K. *Acc. Chem. Res.* **2003**, 36, 95.
(22) Pant, D.; Riter, R. E.; Levinger, N. E. *J. Chem. Phys.* **1998**, *109*, 9995.
(23) Riter, R. E.; Willard, D. M.; Levinger, N. E. *J. Phys. Chem. B* **1998**, *102*, 2705.
(24) Levinger, N. E. *Curr. Opin. Colloid Interface Sci.* **2000**, *5*, 118.
(25) Mittleman, D. M.; Nuss, M. C.; Colvin, V. L. *Chem. Phys. Lett.* **1997**, *275*, 332.
(26) Boyed, J. E.; Briskman, A.; Colvin, V. L. *Phys. Rev. Lett.* **2001**, *87*, 147401.
(27) Boyed, J. E.; Briskman, A.; Sayes, C. M.; Mittleman, D. M.; Colvin, V. L. *J. Phys. Chem. B* **2002**, *106*, 6346.
(28) Hasegawa, M.; Sugiura, T.; Shindo, Y.; Kitahara, A. *Colloids Surf., A* **1996**, *109*, 305.
(29) Datta, A.; Mandal, D.; Pal, S. K.; Bhattacharyya, K. *J. Phys. Chem. B* **1997**, *101*, 10221.

(30) Keh, E.; Valeur, B. *J. Colloid Interface Sci.* **1981**, *79*, 465.
(31) Rio, L. G.; Mejuto, J. C.; Ciri, R.; Blagoeva, I. B.; Leis, J. R.; Ruasse, M. F. *J. Phys. Chem. B* **1999**, *103*, 4997.
(32) Oster, G.; Nishijima, Y. *J. Am. Chem. Soc.* **1956**, *78*, 1581.
(33) Gautam, P.; Harriman, A. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 697.
(34) Ito, K.; Mutoh, M.; Harata, A.; Sawada, T. *Chem. Phys. Lett.* **1997**, *275*, 349.
(35) Furui, G.; Ito, K.; Tsuyumoto, I.; Harata, A.; Sawada, T. *J. Phys. Chem. A* **1999**, *103*, 7575.
(36) Hirose, Y.; Yui, H.; Fujinami, M.; Sawada, T. *Chem. Phys. Lett.* **2001**, *341*, 29.
(37) Takei, M.; Yui, H.; Hirose, Y.; Sawada, T. *J. Phys. Chem. A* **2001**, *105*, 11395.
(38) Yui, H.; Takei, M.; Hirose, Y.; Sawada, T. *Rev. Sci. Instrum.* **2003**, *74*, 907.
(39) Terazima, M. *Chem. Phys. Lett.* **1994**, *230*, 87.
(40) Terazima, M. *J. Chem. Phys.* **1996**, *105*, 6587.
(41) Terazima, M.; Hara, T.; Hirota, N. *J. Phys. Chem.* **1993**, *97*, 10554.
(42) Terazima, M.; Hirota, N. *J. Chem. Phys.* **1994**, *100*, 2481.
(43) Terazima, M. *Chem. Phys.* **1994**, *189*, 793.
(44) Conrad, R. H.; Heitz, J. R.; Brand, L. *Biochemistry* **1970**, *9*, 1540.
(45) Martin, M. M.; Plaza, P.; Changenet, P.; Meyer, Y. H. *J. Photochem. Photobio. A* **1997**, *105*, 197.
(46) Changenet, P.; Zhang, H.; van der Meer, M. J.; Glasbeek, M.; Plaza, P.; Martin, M. M. *J. Phys. Chem. A* **1998**, *102*, 6716.
(47) van der Meer, M. J.; Zhang, H.; Glasbeek, M. *J. Chem. Phys.* **2000**, *112*, 2878.
(48) Glasbeek, M.; Zhang, H.; van der Meer, M. J. *J. Mol. Liq.* **2000**, *86*, 123.
(49) Yoshihara, K. *Adv. Chem. Phys.* **1999**, *107*, 371.
(50) Jimenez, R.; Fleming, G. R.; Kumar, P. V.; Maroncelli, M. *Nature* **1994**, *369*, 471.
(51) Horng, M. L.; Gardecki, J. A.; Papazyan, A.; Maroncelli, M. *J. Phys. Chem.* **1995**, *99*, 17311.