2P042 Solvation Process of Electron Generated in Non-Polar Part of Micellar Solution Observed with Femtosecond Time-Resolved Near-Infrared Spectroscopy

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Introduction

Solvated electrons are important in solution photochemistry and photoelectrochemistry. The study of solvated electron has been an interesting area since the first observation of solvated electrons in liquid ammonia in 1864. The discovery of the aqueous solvated electron in 1960' has inspired many experimental and theoretical studies about the solvated electron.^[1]

The spectral properties of the solvated electrons are strongly dependent on the surrounding medium, which makes the electrons an ideal probe for studying solvation process in polar and non-polar solvents. Unlike ordinary solutions, micellar solutions have both polar and non-polar domains. In micellar solutions, surfactant molecules form micelles in which the hydrophobic parts of the surfactants are assembled inside while the hydrophilic parts act as the interface with the water phase. It is widely accepted that the hydrophobic molecules are solubilized in the hydrophobic part of the micelle.^[2] In this case the solvent participating in the solvation process are the hydrophobic parts of the surfactants.

Although many researchers have been studying the micellar solutions, the structure of the micelles and the interaction between a solubilized molecule and the surrounding surfactant molecules have not been fully understood.

We study the solvation process of electrons generated in a sodium dodecyl sulfate (SDS) micellar solution with femtosecond time-resolved near-infrared spectroscopy at 950-1550 nm. Excess electrons generated after excitation of *trans*-stilbene in the non-polar part of the micellar solution present a broad absorption band centered at about 1200 nm at early time delays. This band disappears after 300 ps. For comparison, solvation process of electrons generated in a dodecane solution, which has a similar salvation environments with the hydrophobic part of SDS, is also studied.

Experimental

Time-resolved near-infrared spectra were measured with a conventional pump-probe method. In short, femtosecond light pulses from a Ti:sapphire regenerative amplifier (800 nm, 1 kHz, 40 fs, 3 W, Coherent Legend Elite) were divided into two parts. A small portion was focused onto a sapphire plate where a white light continuum was generated. The near-infrared portion of the white light was used as the probe pulse. The remaining large portion was used to pump an OPA (OPerA Solo) for generating the pump pulse (1 kHz, 5-6 mW, 300 nm). The beam diameter at the sample was 200 µm. The probe light that passed the sample was analyzed by a spectrograph (Oriel MS127i) and was detected by a linear InGaAs array detector (256 channels, Hamamatsu G8162-256S). Fluctuation of the probe light was used for correcting the wavelength-dependent shift of the time origin caused by the group velocity dispersion.

A mixture of 40 mg of *trans*-stilbene, 8 g of SDS and 100 mL of water was sonicated for the preparation of a micellar solution. A small amount of undissolved *trans*-stilbene was filtered off. For comparison, another two solutions, 40 mg of *trans*-stilbene mixed with 100 mL of dodecane, and 8 g of SDS mixed with 100mL of water, were used as the samples as well. The sample was flowed through a quartz cell (1 mm) by a magnetic gear pump for the measurement.

Sodium dodecyl sulfate and dodecane were purchased from Sigma-Aldrich. *Trans*-stilbene was purchased from Wako Chemicals. They were used as received. Water was ion exchanged and then distilled before used for preparing micellar solutions.

Results and discussion

Absorbance changes of *trans*-stilbene induced by excitation at 300 nm were recorded by time-resolved near-infrared spectrometer. The transient spectra of *trans*-stilbene at the time delay of 0, 0.13, 0.4, 5.2, 205 and 358 ps in the SDS micellar solution and in the dodecane solution are shown in Figure 1(b) and Figure 1(c), respectively. Absorbance changes of SDS solution excitated at 300 nm were also recorded and are shown in Figure 1(a).



Figure 1: Time-resolved near-infrared absorption spectra of (a) SDS solution, (b) *trans*-stilbene in SDS solution and (c) *trans*-stilbene in dodecane, measured with photoexcitation at 300 nm.

In Figure 1(b), the observed absorption spectra of *trans*-stilbene show broad features including two components in the wavelength region from 950 to 1550 nm. One component at the shorter wavelength side in Figure 1(a) and Figure 1(b) comes from the aqueous solvated electrons which are shown a broad band centered at 720 nm.^[3] The other component centered at 1200 nm can be assigned to the electrons generated in the non-polar part of the micelle. The transient absorption spectra of *trans*-stilbene in dodecane (Figure 1(c)) also have the band centered at 1200 nm. The solvation environment of *trans*-stilbene in the SDS micelle is very similar to those in the dodecane solution because the *trans*-stilbene molecules in the micelle are surrounded by dodecyl groups. The lifetime of electrons generated in the non-polar part of micelle is more than 300 ps.

References

- [1] Y. Kimura, J. C. Alfono, P. K. Walhout, P. F. Barbara, J. Phys. Chem. 98 (1994), 3450.
- [2] K. Iwata, H. Hamaguchi, J. Raman Spectrosc. 29 (1998), 915.
- [3] P.J.Reid, C. Silva, P.K. Walout, P. F. Barbara, Chem. Phys. Lett 228 (1994), 658.