Solvation Dynamics at the Water/Mica Interface as Studied by Time-resolved Fluorescence Spectroscopy

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Solvation dynamics at the water/mica interface was investigated by time-resolved fluorescence spectroscopy. Time-resolved fluorescence spectra of a coumarin dye immobilized on the mica surface show dynamic Stokes shifts with several hundreds picosecond time scale. Solvent relaxation time observed at the water/mica interface was remarkably longer than that observed in a bulk solution, suggesting existence of a rigid water layer on the mica surface, that is, hydrogen-bonding network is strongly formed at the mica surface.

Physical and chemical properties of liquid/solid and liquid/liquid interfaces have attracted much attention because of their importance in both fundamental sciences and practical applications.[1,2] Among the properties of interfaces, solvation of molecules at interfaces has been one of the subjects to be clarified, because it affects the absorptivity and reactivity of molecules at interfaces.[2–7] Solvation dynamics at the interfacial region has been paid little attention, although it is critical to address the fundamental problems in the interfacial phenomena. Existence of ultrafast solvation dynamics within a few ps was revealed by time-resolved second harmonic generation at the liquid/silica interface,[8] whereas a slow rate of the solvent relaxation, ca. 100 ps, was reported for the butanol/sapphire interface by time-resolved fluorescence spectroscopy.[9] In these experiments, organic solvents were used as a liquid phase and solvation dynamics was examined using probe molecules adsorbed physically on the solid substrates. In the report on solvation dynamics at the butanol/sapphire interface,[8] time-resolved fluorescence spectra could not be obtained because of the extremely weak intensity of fluorescence. In the present study, solvation dynamics is examined at the water/mica interface using a coumarin dye as a probe molecule by time-resolved fluorescence spectroscopy, where the probe molecule is chemically immobilized on the atomically flat mica surface. As for the water/mica interface, water molecules have been reported to condense on the mica surface forming a solid-like ice layer based on the measurements of scanning polarization force microscopy,[10] and the two-dimensional ice-like network through hydrogen bondings has been proposed by first principle molecular dynamics simulations.[11] Thus, it is interesting to examine the effect of the ice-like layer on the solvation dynamics of molecules at the liquid/mica interface.

The mica substrate modified by a propylamide coumarin 343 (PAC-343) dye was prepared by a coupling reaction of coumarin 343 succinimidyl ester with propylamine immobilized on the mica surface. Immobilization of propylamine was carried out by immersing the mica substrate into an aqueous solution of triethoxyaminopropylsilane. Surface concentration of PAC-343 was estimated as 3.4×10^{12} molecules cm^{-2} from absorption measurements, and this value corresponds to the occupied area of 21 nm^2/molecule assuming the molecular dimension of PAC-343 as 1 nm^2/molecule. The mica substrate was placed vertically in a 1 cm quartz cuvette filled with a solvent which was a mixture of EtOH and water. To examine the solvation dynamics of a coumarin dye in a bulk solution, propyl amide coumarin 343 was synthesized and its fluorescent characteristics are compared with those obtained at the liquid/mica interface. The experimental set up for time-resolved fluorescence spectroscopy was described previously.[12–14] The second harmonic (390 nm) of a 100 fs Ti:sapphire laser (Spectra Physics) was used as an excitation source and fluorescence was detected by a streak scope (Hamamatsu model C4334). The maximum time-resolution of the present system was approximately 60 ps at 5 ns full scale.

Fluorescence spectra of PAC-343 immobilized on the mica surface and in a bulk solution were measured using a mixed solvent of EtOH and water with different mixture ratios. The wavelength of fluorescence maximum showed a red shift with increasing the mole fraction of water in both cases of the mica interface and bulk solution as shown in Figure 1. It is well known that the fluorescence maximum of coumarin dyes shifts to red as the solvent polarity increases.[15] Accordingly, the results shown in Figure 1 indicate that the amount of water molecules in a solvation shell surrounding a PAC-343 molecule increases as the mole fraction of water increases.

Time-resolved fluorescence spectra of PAC-343 were measured to obtain detailed information on solvation dynamics at the liquid/mica interface, and the shift of fluorescence maximum to red, that is dynamic Stokes shift, was observed during the time course of emission. A noticeable difference in bandwidth was not observed in the time-resolved fluorescence spectra and the dynamic Stokes shift can be attributed to the solvent relaxation, since the fluorescence maximum of coumarin 343 is well known to reflect the solvent polarity.[15]

The fluorescence maximum was obtained by the best fit of the experimental data to a log-normal formula.[16] The wavenum-

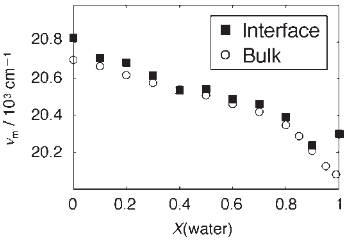

Figure 1. Variation of the wavelength values of average fluorescence maximum in bulk solutions and at the liquid/mica interface as a function of the water mole fraction in an EtOH–water mixture system. *X*(water) represents the water mole fraction.

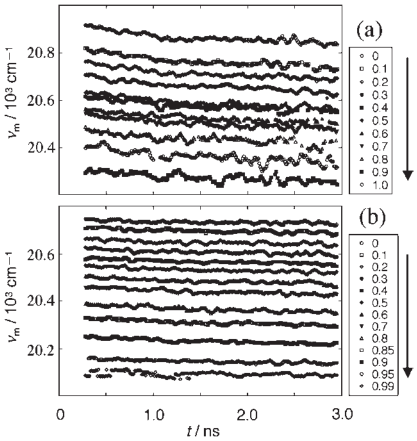

Figure 2. Time-dependent spectral shifts found (a) at the liquid/mica and (b) in the bulk phase. The water mole fractions are given on the right.

ber of the fluorescence maximum was plotted as a function of time, and the results obtained at the liquid/mica interface and in a bulk solution are shown in Figure 2. As shown in Figure 2a, dynamic Stokes shift, which can be ascribed to the solvent relaxation, was observed at the liquid/mica interface, whereas hardly any solvent relaxation can be recognized in a bulk solution as shown in Figure 2b. Although it has been reported from a fluorescence up-conversion study that ordinary water molecules in a bulk solution exhibit solvation dynamics on a sub-picosecond time scale,[15] considerably slow solvation dynamics was observed in the present study, suggesting the remarkable difference in microenvironment at the liquid/mica interface compared with the bulk solution.

The fluorescence maximum of the time-dependent spectrum $\nu_m(t)$ can be assumed to shift to lower energy in an exponential fashion with solvent relaxation time τ_s and it is expressed by the following equation:[16,17]

$$\nu_m(t) = (\nu_m(0) - \nu_m(\infty))e^{-t/\tau_s} + \nu_m(\infty), \tag{1}$$

where $\nu_m(0)$ and $\nu_m(\infty)$ represent the fluorescence maxima of the initially excited and relaxed states, respectively. The plots in Figure 2a can be fitted by Eq 1 and the solvent relaxation time τ_s is estimated. Figure 3 shows τ_s as a function of a mole fraction of water, and it can be seen that τ_s increases as the mole fraction of water increases. It has been known that a coumarine molecule shows a long lifetime and a blue shift of the fluorescence maximum.[15,18] Accordingly, above mole fraction dependence of the solvent relaxation time can be explained in terms of hydrogen-bonding network formation at the liquid/mica interface.

The surface of mica is hydrophilic, and a ice-like water monolayer has been reported to form at the water vapor/mica interface when the humidity becomes to be ca. 90% based on the SFG measurements.[19] Formation of thick adsorption layer of ethanol clusters has also been reported at the cyclohexane–ethanol binary liquid/silicon oxide interface.[20] When protic solvents form clusters at the liquid/solid interface, the viscosity in the vicinity of the liquid/solid interface is expected to increase. This increase in the viscosity should be the cause of slow solvation dynamics of PAC-343, which is immobilized on the mica surface, observed in the present study. Increase in the solvent relaxation time τ_s at the larger mole fraction of water reflects the higher viscosity at the water/mica interface, suggesting the growing of rigid hydrogen-bonding network at the water/mica interface.

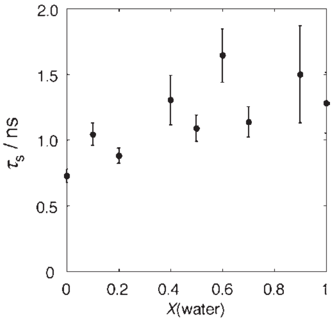

Figure 3. Plots of solvent relaxation time τ_s at the liquid/mica interface as a function of the water mole fraction in an EtOH–water mixture system.

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