

Hydration Characteristics of a Water Pool in a Nano-Confined System Probed by a Superphotoacid

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The reverse micellar system is a representative biomimetic molecular system. A reverse micelle consists of a non-polar solvent phase, an interfacial region of surfactant molecular layer and a water pool [1]. The characteristics of a reverse micelle system varies with the size of the reverse micelle, mainly the size of the water pool confined in a nanometer core. The water nanopool can be further distinguished as two different regions; boundary water and free water. In the boundary water region, the water molecules have strong dipole-ion interaction with the surfactant head groups, so the boundary water motion is more restricted than free water motion [2, 3]. The motion of water molecules in the free water region becomes similar with that of bulk water.

Here, we investigated the hydration characteristics of a water pool in the Aerosol-OT (sodium bis[2-ethylhexyl] sulfosuccinate) reverse micelle by measuring the fluorescence of cationic superphotoacid, N-methyl-7-hydroxyquinolinium (NM7HQ⁺) ion in a water nanopool. NM7HQ⁺ is a strong photoacid with a much lower pKa value when excited by light than in the ground state which triggers the excited-state deprotonation of the cationic NM7HQ⁺ (C) giving birth to a product, keto form (K). The two prototropic species have different formal charges, which affect residence sites and diffusive motions in the confined environment of the reverse micelle.

The excited-state dynamics of NM7HQ⁺ was analyzed by measuring picosecond-resolved emission spectra (TRES). The spectral deconvolution of the TRES into the spectra of the two prototropic species allowed for the differentiation of the spectral shift from the excited-state population dynamics. As a result, we could successfully resolve the hydration dynamics in the water pool and correlate it to proton-transfer dynamics. Also, the time-dependent fluorescence anisotropy measurements revealed the rotational diffusion dynamics of the two prototropic species.

References

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