Kinetics of Excited State Proton Transfer in Aqueous Reverse Micelles

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Proton transfer, the movement of a proton from a donor atom (the acid) to an acceptor atom (the base), is one of the most fundamental and important chemical reaction. In the Takematsu lab we are interested in the factors which influence the kinetics, or rate, of these reactions. The goal of my project this summer was to use water pockets called reverse micelles to simulate the conditions under which such reactions commonly occur in biological systems. A reverse micelle consists of three layers: a large amount of nonpolar solvent forms the outermost layer, followed by a layer of surfactant molecules which form the barrier between the nonpolar solvent, hexane, and the innermost layer, which consists of the polar solvent, the water core of the reverse micelle. The surfactant is an amphiphilic molecule, consisting of a long, nonpolar hydrophobic tail and a charged hydrophilic head. The surfactant molecules arrange themselves in a spherical layer with the hydrophobic tails facing outwards, and the hydrophilic heads facing inwards, allowing each end to interact favorably with the proper solvent.

We insert a molecule into the water core of the reverse micelle by rigorous manual mixing or by sonication. The molecule is contained in a space several Angstroms wide, which can affect the proton transfer dynamics by limiting the number of water molecules available to solvate the diffusing proton. This molecule-in-micelle system is designed to mimic an organic molecule bound inside a small protein cavity, a common situation in biological systems. To study the kinetics of proton transfer in confined spaces, we choose a molecule known as a photoacid, which is not a strong acid at biological pH, but upon UV excitation undergoes a shift in electron density, lowering the pKₐ and thus increasing the acidity. The advantage of using a photoacid is that we are able to use the excitation as a ‘trigger’ for the proton transfer event, and being able to start it on command is crucial to understanding the rate of the reaction. We control the micellar radius by varying the proportions of water and surfactant, allowing us to study the effects of cavity size on acid-base chemistry.

The photoacid I worked with this summer was 2-naphthol-6,8-disulfonate (2N68DS). The photoacid-micelle system was analyzed using both fluorescence and UV-vis spectroscopy as the acid and base forms of 2N68DS have distinct spectroscopic profiles. We varied the size of the micelles and then monitored the change in the spectra to determine the quantity of acid and base present in solution. To measure the rate of proton transfer in the excited state, we used a time resolved spectroscopic technique called time correlated single photon counting. In TCSPE a laser repeatedly excites a sample, and for each excitation event the detector records a single photon at some time after the excitation. By collecting a high number of photons, the decay profile of the emission of the sample can be assembled. After collecting the data we used the software DAS6 Analysis to fit the decay profiles to exponential curves and extracted the lifetimes of the decay. As a control, the experiments were also done on 2N68DS samples in bulk water.

From our experiments we found that as the micellar radius is decreased the rate of decay of the acid form generally decreases. As fewer water molecules are available to solvate the diffusing proton, the kinetics of the reaction slow down. We attribute this to the effects of the polar surfactant heads inducing a quasi-ordered layer of water molecules to form near the surfactant-water interface. This means that the solvation of a proton is slowed because the quasi-ordered water molecules must break their interactions with each other before the proton can be fully solvated. When the micelle is sufficiently large, the photoacid is far enough away from the interface that it can be treated as being in bulk water. In addition to the kinetics study, we refined the process of creating and observing the micelles. While several literature sources describe using sonication to induce the micelles to take up the photoacid, we showed that sonication may induce changes in the concentrations of micelle components by evaporating the nonpolar solvent. We found that thorough mixing by hand allowed for sufficient uptake and did not induce unwanted changes in the solutions.

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Funded by the Coles Fellowship