

KINETIC STUDIES OF FAST REACTIONS AT WATER-MICELLE INTERFACES

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Micellar dispersions have frequently been used to model the changes in diffusional and reactivity properties of substrates associated with biological supramolecular assemblies such as cell membranes. Our approach has been to use electron beam and laser generation of short-lived transients with detection by time-resolved spectroscopy to observe the effects of micellar phases on simple physicochemical processes such as collisional quenching and electron transfer.

When molecules of pyrene (or other aromatic fluorescent probes) solubilized by the lipid region of surfactant micelles are excited to the S_1 state by an ultraviolet laser pulse, the decay rate of the fluorescence is critically dependent on the nature and concentration of counter-ions in the diffuse double layer. For some ions (e.g., Cs^+ , Ag^+) the rate law for decay is exponential; for other ions (Cu^{++} , dimethyl viologen) a complex decay is observed that becomes exponential at long times. The initial rate of the early component is dependent on the quencher concentration; the exponential part is concentration independent.

A model that leads to an understanding of this phenomenon has been developed, based on quenching interactions occurring at interfacial collisions. Using the notion of quencher ions distributing themselves among micelle double layers according to a Poisson function, a mathematical analysis leads to the expression $N^*(t) = N^*(0) \cdot \exp\{\langle r \rangle e^{-t/\tau_1} - \langle r \rangle - t/\tau_0\}$, where $N^*(t)$ and $N^*(0)$ refer to the concentration of pyrene S_1 states at times t and zero after the excitation pulse, $\langle r \rangle$ is the mean value of the occupancy index, and τ_0 and τ_1 are the S_1 natural lifetimes for pyrene in micelles associated with zero and one quencher, respectively. This expression describes the observed complex cases adequately. The simple exponential rates can be understood in terms of weaker micelle-ion binding, causing a nonstatic ion population about micelles that leads to a time-averaged decay rate being observed.

This variability in micelle-ion association strength is supported by electron pulse radiolysis measurements of the rate of reaction of hydrated electrons with e.g., dimethyl viologen cations. When the concentration of surfactant molecules is raised above the critical micelle concentration, the rate constant for electron capture falls, consistent with the idea that such cations are associated with micelles in a quasi-static distribution, at least for several microseconds. Details of the concentration dependence lead to consideration of the primary salt effect associated with micellar reactions.

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