Reaction Kinetics in Micelles

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Reactions in self-aggregated assemblies of amphiphilic molecules, such as micelles, have attracted growing interest mainly for two reasons. First, proper organization of reactants by their solubilization in suitable micro-heterogeneous environments enables one to catalyze and control a wide variety of practically important reactions. On the other hand, simple indicator processes may serve as a tool to investigate the embedding structures themselves. Although open to different interpretations, sometimes ambiguous, such methods provide information of exceptional value on grounds different from other experimental techniques, such as scattering.

As the spatial scales are important in formulating the thermodynamics of self-aggregated structures, the time scales are of equal importance in the formulation of the reaction kinetics in such systems. While the micellar aggregates are thermodynamically stable, they are dynamic structures displaying complex formation-breakdown processes that give rise to intermicellar migration of solubilized molecules so that the number of reactants in a micelle continuously fluctuates. Since the average number of guest species per micelle is typically low and comparable to the fluctuation, the occupation statistics is very important in such systems and a deterministic model of kinetics, which considers only the average, cannot be applied. The basic idea in analyzing reaction kinetics in micelles is to separately consider the process within a finite volume and then take the occupation statistics and the dynamics of reactant exchange into account.

Let us consider diffusion-controlled luminescence quenching as a typical example of reaction. Normally the number of excited-state probes is sufficiently low to neglect there interference. The excited state survival probability in a finite volume in the presence of n diffusing quenchers is approximately exponential, $\Phi_n(t) \simeq \exp[-(1/\tau+nk_q)t]$, with the rate constant k_q depending on the micelle radius, diffusion coefficients of reactants, their size and spatial arrangement; τ denotes self-decay lifetime. When reaction is considerably faster than solubilizate exchange, each micelle acts as a cage, and the overall kinetics can be obtained by averaging the microscopic intramicellar kinetics

with a given number of reactants, $\Phi_n(t)$, over the equilibrium statistical distribution of reactants among the micelles, P_n. The equilibrium distribution is determined by molecular interactions. It the simplest case, it obeys Poissonian statistics, $P_n = (\bar{n}^n/n!)\exp(-\bar{n})$, where $\bar{n}$ is the average number of quenchers per micelle. Averaging over P_n we obtain the observable survival probability, $\ln \Phi(t) = -t/\tau - \bar{n}[1 - \exp(-k_q t)]$.

Solubilizate exchange can be approximately described by the first-order rate constant, k_-, obtained by solving the diffusive barrier-crossing problem. Micelles can be characterized by a deep potential well with a certain barrier at the interface. k_- is then determined approximately by diffusion of free solutes away from the micelle. Assuming that probes are fully solubilized in micelles while quenchers are allowed to migrate during the excitation lifetime via a one-particle mechanism, one can develop a stochastic model for luminescence quenching which yields the following result for the ensemble-averaged survival probability, $\ln \Phi(t) = -A_1 - A_2[1 - \exp(-A_3)]$, where $A_1 = \tau^{-1} + \bar{n}k_- k_q/(k_- + k_q)$, $A_2 = \bar{n}k_q^2/(k_- + k_q)^2$, and $A_3 = k_- + k_q$. It is possible to include many important additional features into the stochastic model, such as probe migration, limited solubilization capability of a micelle, polidispersity, multiple occupancy of excited probes, many-particle exchange mechanism, back reaction, etc.

Under certain conditions (temperature, concentration) micelles can form clusters while retaining their individual closed structure. Reaction kinetics in micellar clusters is described on the basis of the continuous-time random walk approach. The survival probability is expresses in terms of the hopping time distribution function, quenching time distribution function, and the generating function of the walk on the underlying lattice. Dimensionality d of the cluster governs the long-time kinetics. For $d > 2$, the long-time behavior is exponential. Loose clusters with $d < 2$ show stretched exponential behavior. Finite clusters exhibit dynamic scaling, i.e., at long times, when all the sites are explored, clusters act as individual micelles where the decay function is given by $\ln \Phi(t) \sim -t/\tau - \bar{n}[1 - \exp(-k_q t)]$ but with renormalized $\bar{n}$ and k_q.

References

[1] A.V. Barzykin and M. Tachiya, Heterog. Chem. Rev. **3** (1996) 105-167.