Fluorescence Experiment 2: Diffusion Controlled Reactions

Overview

In this experiment you will measure the fluorescence lifetime of anthracene in solution using a time correlated single photon counter. You will then perform a Stern-Volmer experiment adding various different concentrations of quencher to the anthracene solution in order to monitor the effect on the lifetime. You will then derive the quenching constant and determine whether quenching is diffusion controlled. You will subsequently repeat the experiment in a more viscous solvent. Finally, you will compare the effect of viscosity on the limiting quenching rate in each solvent and assess whether quenching agrees with the theory of diffusion-limited reactions.

Version 1.0

Diffusion Controlled Reactions

Introduction

Consider the general bimolecular reaction in solution, below, where reactants, A and B, produce products C and D:

$$A \quad + \quad B \xrightarrow{k_D} (A\text{---}B) \xrightarrow{k_R} C \quad + \quad D$$

The reaction can be considered as a two stage process: first diffusion of reactants A and B with a rate constant[1] k_D, occurs until they encounter one another. This is followed by rapid chemical reaction via rate constant, k_R to form products. Clearly, it is the rate of stage one which limits the overall reaction rate[1].

If the molecules in the system are assumed to be spherical, it is possible to estimate k_D, which is the rate constant at the diffusion controlled limit. The magnitude of k_D ultimately determines how fast a reaction will occur in a given solvent.

The elementary diffusion controlled reaction between A and B to give products is therefore given by

$$k_D = 4\pi N_A (r_A + r_B)(D_A + D_B)$$

where N_A is Avogadros number, D_A and D_B are the diffusion coefficients and r_A and r_B are the radii of the spheres, A and B. If it is assumed that A and B are the same size (i.e., $r_A = r_B = r$) and that $D_A = D_B = D$, then

$$k_D = 4\,\pi\,N_A\,2\,r\;x\;2\,D$$

By using the Stokes-Einstein equation

$$D = \frac{kT}{6\,\pi\,\eta\,r}$$

where η is the viscosity of the solvent

it is subsequently possible to derive the diffusion limited rate constant

$$k_D = \frac{8\,R\,T}{3\,\eta}$$

For a diffusion-controlled process, the rate of reaction, at a given temperature, is therefore inversely proportional to η.

Fluorescence[2] quenching[3] is one experimental method for estimating the diffusion controlled rate limit of a solvent. Here a small molecule quencher[3] (Q) and a fluorescent excited state species (M*)[2] in solution, diffuse together, until they encounter one another. Q then, deactivates M* by collision which returns M* to the ground state by transferring its energy to Q as shown below

$$M^* + Q \xrightarrow{k_q} M + Q^*$$

The bimolecular quenching constant[3], k_q will consequently depend on the viscosity of the solvent. A knowledge of k_q will allow estimation of the diffusion controlled rate constant since

$$k_q \approx k_D$$

Since Q is usually non-fluorescent this results in a decrease in the fluorescence[2] properties of the system such as the quantum yield[2], fluorescence lifetime[2] (τ) and intensity[2] as the quencher[3] concentration increases. The process whereby one quencher collides and deactivates one excited state species is known as dynamic quenching and follows Stern-Volmer kinetics[3].

The Stern-Volmer equation[3] relates, for example, the fluorescence lifetime[2] in the absence (τ^o) and presence (τ) of some concentration of Q

$$\frac{\tau^o}{\tau} = 1 + k_q \, \tau^o \, [Q]$$

and allows experimental estimation of k_q and hence k_D.

Aims

You will make up a dilute solution of anthracene (see Figure 1 for the chemical structure) in two solvents of different viscosity: toluene [η = 0.585 cP (25 °C)]; triacetin [η = 2.52 cP (25°C)]The absorbance and fluorescence emission spectra should be recorded in each solvent. Using the single photon counter[4], you will determine the τ^o of anthracene in toluene and tracetin, respectively.

Subsequently, you will make up a series of dilute solutions of anthracene in toluene with increasing amounts of quencher (CH_3NO_2). By measuring τ at each concentration of Q and using the Stern-Volmer relationship you will determine k_q and hence k_D. Subsequently, this procedure will be repeated in triacetin. Finally, you will compare the effect of viscosity on the limiting rate for the process in each solvent. Do your observations agree with the theory of diffusion-limited reactions?

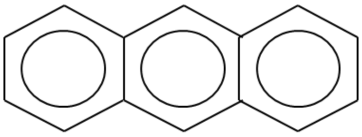

Figure 1: Structure of anthracene