

Photophysics in a Disco

Luminescence Quenching of Quinine

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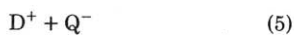
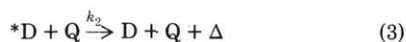
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Luminescence experiments are colorful, dramatic, and can be very popular with students. However, sophisticated instrumentation or lasers (necessary for some experiments) are not always available. In this paper we describe a simple procedure for semiquantitatively examining luminescence quenching that can be performed using the "chemicals" and "equipment" found in many discos: tonic water, table salt, a shot glass, volumetric glassware (glasses), and a black light. The experiment can also be performed quantitatively if a filter fluorimeter or spectrofluorimeter is available. It demonstrates a number of features of luminescence and can be used as the basis for a number of discussions or student special projects.

Background and Theory

Quinine, the bitter component of tonic water, is a highly fluorescent, organic molecule that has been widely used as a luminescence quantum-yield standard (1). The compound is stable in solution and emits blue light when it is excited in the near UV. Unlike many other luminescent molecules, its emission is not quenched by oxygen; however, it is quite susceptible to halide quenching. Because of this property, solutions of quinine and Cl^- are useful as fluorescence lifetime standards (2), and quinine is used in the microassay of halides in combusted organic materials (3).

If a glass of tonic water is held under a black light, an intense quinine emission is easily observed. Addition of table salt results in a decrease in luminescence intensity (quenching). The following discussion is intended for those conversant in chemical kinetics and will have to be suitably tailored for the students doing the experiment. Stern and Volmer described this type of quenching as a bimolecular process that competes with radiative decay, and derived an equation to express the phenomenon (4). Their equation was based on the following kinetic scheme:



where D is the ground-state species, *D is the excited-state species, and Q is the quencher. k_1 is the first-order rate constant for decay of the excited state (eq 2), and k_2 is the sum of the bimolecular rate constants for all processes depleting the excited state including catalytic deactivation (eq 3), energy transfer (eq 4), and electron transfer (eqs 5, 6). These equations yield (5)

$$I_0/I = 1 + K_{sv}[\text{Q}] \quad (7)$$

where I_0 is the luminescence intensity of the solution in the absence of quencher, I is the intensity at quencher concentration [Q], and K_{sv} is the Stern-Volmer quenching constant. The Stern-Volmer constant can be expressed in terms of the bimolecular quenching constant k_2 and τ_0 , the lifetime of the luminescent species in the absence of quencher. For our disco experiment, we use the alternative definition, k_{fc} , in honor of our salt supplier Kentucky Fried Chicken,

$$K_{sv} = k_2\tau_0 \quad (8)$$

$$K_{sv} = k_{fc}\tau_0 \quad (9)$$

$$\tau_0 = 1/k_1 \quad (10)$$

If a plot of $I_0/I - 1$ vs. [Q] is constructed, the data should be linear with a slope equal to K_{sv} . If τ_0 is known, k_2 or k_{fc} is easily calculated from eqs 8 and 9. Studies of the Cl^- quenching of quinine show that linearity is maintained up to at least $I_0/I = 100$ in 0.1 N H_2SO_4 (2a).

Quenching Measurements

The main problem is how to determine the intensity of the quenched sample relative to the unquenched one without instrumentation. We choose to do this by exploiting the fact that for an optically dilute sample (absorbance less than about 0.1) the emission intensity is directly proportional to the concentration. By making a series of quantitative dilutions of a quinine solution, one has a series of graded emission standards with known relative brightness compared to the unquenched reference. Then, by making visual comparisons between the quenched samples and the diluted ones we can estimate the degree of quenching.

Standards were made up by first diluting pure tonic water 1 to 10 with tap water to yield our working stock solution of quinine; this was necessary to bring the quinine absorbance down to about 0.1/cm. This stock solution was then diluted with a shot glass to give standards with weaker emissions. We made solutions that were 12.5%, 25%, 33%, 50%, and 75% as concentrated as the stock. For example, the 25% sample was made by mixing half a shot of the stock solution with one and a half shots of tap water. These solutions were then set out in the same size test tubes (or shot glasses in a disco) under the black light.

Quenched samples were made by dissolving sodium chloride in the stock quinine solution and mixing varying amounts of the unquenched stock solution with the quenched one. Because there are no scales or graduated cylinders in discos, we employed the little twin salt packs used in restaurants. As there is no standardized unit for this, we adopted non-SI units with one tube of a twin pack equaling one Morton and the unit of volume being the Shot. Our series of salt-quenched tonic water solutions are shown in Table 1.

The luminescence intensities are determined by compar-

Table 1. Tonic Water Solutions for Determining k_{fc}

Salt Solutions (Morton/Shot)	Composition	
	shots of stock salt solution	shots of stock tonic water
0.031	1/4	3 & 3/4
0.063	1/2	3 & 1/2
0.125	1	3
0.250	1	1
0.375	3	1
0.500	1	0

^a 1 shot = 38 mL.

^b 1 Morton = 1/2 packet of Kentucky Fried Chicken salt = 0.2958 g of NaCl.

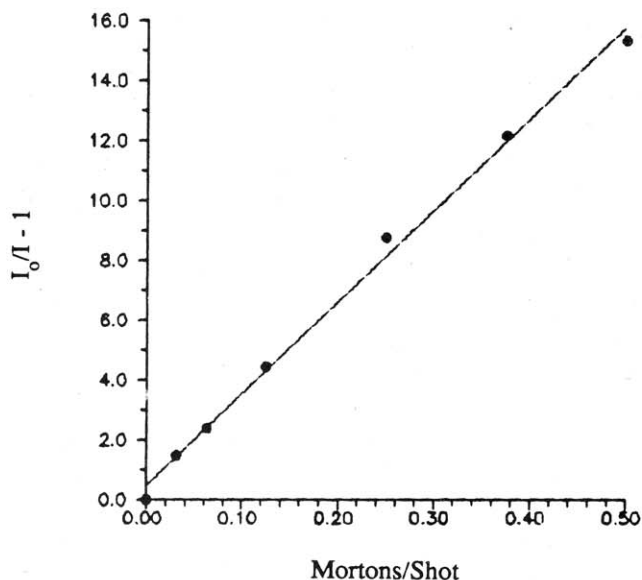


Figure 1. Luminescence intensity quenching plot for tonic water in disco units. Intensities were determined visually. The solid line is a polynomial fit, but the coefficients have no physical significance.

ing the diluted solutions with the quenched ones. For example, a quenched solution having an intensity midway between our 50% and 25% diluted stocks would be estimated as equivalent to a 38% dilution, and thus would have an I_0/I of 2.6 ($1/0.38$). While this procedure seems crude, agreement between different viewers was typically 5–10%.

Figure 1 shows a quenching experiment done entirely with visual comparison and dilutions with a shot glass. Clearly, the quenching curve is not linear as predicted by eq 7. Using the early linear portion of the curve, the K_{sv} is 18 Shot/Morton. Based on the widely measured lifetime of quinine sulfate of 20 ns, the k_{fc} is 1×10^9 Shot-Morton $^{-1}$ -s $^{-1}$. We return later to the explanation of the nonlinearity, which demonstrates important aspects of luminescence spectroscopy.

More quantitative quenching data were obtained by using an emission spectrometer (SPEX Fluorolog). The sample was excited at 350 nm, and the emission intensity was measured at the fluorescence maximum (450 nm). For the concentrations of quinine and salt suggested in Table 1, blank subtraction was not necessary.

Figure 2 is a Stern–Volmer plot of data obtained using Giant brand tonic water. The slope of the best fit line, K_{sv} , is 30.7 Shot/Morton or 231 M $^{-1}$ at 23 °C.

Since tonic water is not pure quinine, lifetimes (τ_0) for five different brands of tonic water were measured using an SLM 48000 multiple-frequency lifetime spectrofluorometer. The

Table 2. Quinine Luminescence Lifetimes (τ)

Brand Name	τ (ns)
Golden Crown	19.4
Seagrams	18.8
Giant	18.3
Canada Dry	19.8
Schweppes	18.5

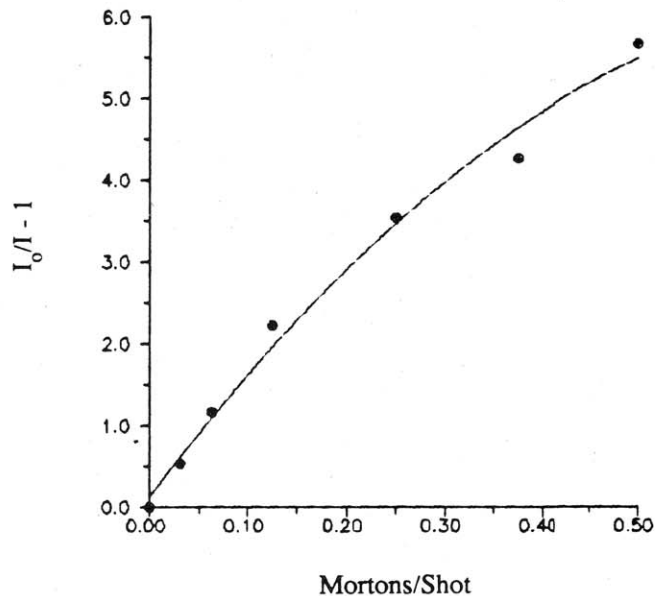


Figure 2. Luminescence intensity quenching plot for tonic water determined on a spectrofluorimeter.

results are tabulated in Table 2 showing that the lifetime is quite insensitive to source. In each case, 1 mL of tonic water was diluted with 10 mL of tap water. These τ_0 's are in agreement with values reported in the literature for quinine in H₂SO₄ (2a, 6).

Using eq 7, k_{fc} is determined to be 1.67×10^9 Shot-Morton $^{-1}$ -s $^{-1}$ or 1.26×10^{10} M $^{-1}$ -s $^{-1}$. Results obtained using reagent NaCl were the same within experimental error as for the salt packets indicating that the additives in the salt packets were innocuous. K_{sv} 's using different sources of quinine were reproducible to $\pm 10\%$, except for Royal Crown brand, which gave a value about 50% higher.

Discussion

This experiment demonstrates the principles of luminescence quenching in a fun way, using ordinary disco or restaurant supplies. Using instrumentation, linear data are obtained for the range of quencher concentrations used, and k_2 values on the order of 10^{10} M $^{-1}$ -s $^{-1}$ indicate that the quenching is near the diffusion-controlled limit.

Literature K_{sv} 's for the Cl $^-$ quenching of quinine range from 87 to 161 M $^{-1}$ (2, 3, 7). These values were obtained from solutions of high ionic strength and acidity, while our K_{sv} 's are measured under much milder conditions. Previous investigations have shown that K_{sv} for the halide quenching of quinine decreases with increasing ionic strength (8). Harty and Rollefson have used the Debye–Hückel theory to analyze the effects of ionic strength on the quenching of quinine by bromide. However, a normal Debye–Hückel equation did not fit the data well, and they presented an empirical expression that did.

Using diluted tonic water results in K_{sv} 's ~ 2 –3 times higher than the literature cited because of the differences in solution environment. The low ionic strength results in

greater effective attraction of the dipositive quinine ion for the Cl^- ions. This results in somewhat more efficient quenching than would be expected for nonelectrostatically assisted diffusion. Interested students might enjoy investigating the effect of adding a nonquenching salt (e.g., KNO_3) to the tonic water solutions.

We turn now to the origin of the nonlinearity of the Stern-Volmer plot of Figure 1. This was traced to the failure of the emission intensities of the diluted solutions to match the dilution factor. In turn, this arose from the variation of solution environment as the quinine was diluted. The intensity of the quinine luminescence is quite dependent on the solution environment, and plots of intensity vs. tonic water concentration turn out not to be linear. We found that adding the proper amount of citric acid (a component of quinine water) to the most dilute quinine solution roughly doubled the emission intensity but had little effect on the emission of the more concentrated quinine. This is exactly the behavior required to give the flattened Stern-Volmer plot of Figure 1. Adding too much acid results in a decrease in emission intensity.

As a check as to whether it was the acidity of the citric acid affecting the luminescence, we found that squeezing fresh lemon into the most dilute solution at first more than doubled the emission intensity but eventually quenched it, while the 35% reference was quenched on the first addition. These results are not completely surprising given the well-known variations in luminescence properties of acids and bases depending on acid concentration and excited-state kinetics. Thus, for reliable intensity standards, the quinine standards would all have to be at the same ionic strength and acidity—which is difficult to do when starting with tonic water.

In spite of the simplicity of the experiment, a large number of possible projects could be derived. For example, given

the effect of lemon juice and citric acid, is the variation in the experiment caused by a simple acidity change or are there specific effects? Is the emission first enhanced by lemon acidity and then quenched by excess chloride? Temperature effects could also be studied. Because τ_0 of quinine is relatively insensitive to temperature (2b), most of the changes in k_{fc} in the latter case could be attributed to changes in the diffusional collision rate.

Iodide is about twice as good a quencher as Cl^- . Thus, the student should be able to determine whether iodized salt would have a different apparent quenching constant than pure chloride. If instrumentation is available, quantitative analysis of mixtures of luminescent species could be done by quenching studies (3).

A complete first-year experiment has been developed. The experiment and student results are available on request.

Acknowledgment

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