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**Short Communication**

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# Study of self-quenching by steady state emission measurements

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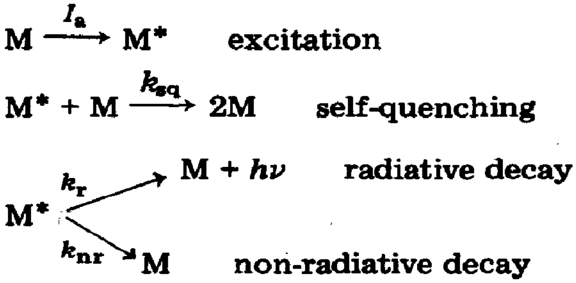
The self-quenching process, namely the quenching of an excited state molecule M* by the same chemical species in the ground state (Scheme 1)



$$\mathrm{M} \xrightarrow{I_a} \mathrm{M}^* \qquad \text{excitation}$$

$$\mathrm{M}^* + \mathrm{M} \xrightarrow{k_{sq}} 2\mathrm{M} \qquad \text{self-quenching}$$

$$\mathrm{M}^* \xrightarrow{k_r} \mathrm{M} + h\nu \qquad \text{radiative decay}$$

$$\mathrm{M}^* \xrightarrow{k_{nr}} \mathrm{M} \qquad \text{non-radiative decay}$$

Scheme 1.

has been generally studied by measuring the lifetime of the excited state as a function of the concentration [1 - 8]. The lifetime $\tau$ and the concentration [M] are related through the following Stern–Volmer-type equation:

$$\tau^{-1} = \tau_\infty^{-1} + k_{sq}[\mathrm{M}] \tag{1}$$

where $\tau_\infty = (k_r + k_{nr})^{-1}$ is the lifetime at infinite dilution and $k_{sq}$ the bimolecular rate constant for the self-quenching. The value of $k_{sq}$ can be determined as the slope of the plot of $\tau^{-1}$ against [M]. The emission yield $\phi$ is also concentration dependent because of the relationship $\phi = k_r\tau$, where $k_r$ is the radiative decay rate constant of the excited state. Accordingly, the following relationship must hold:

$$\frac{\phi_\infty}{\phi} = 1 + k_{sq}\tau_\infty[\mathrm{M}] \tag{2}$$

where $\phi$ is the emission quantum yield when the concentration is [M] and $\phi_\infty$ refers to an infinitely dilute solution. Equation (2) has been used only once previously, to our knowledge, in the literature [6], probably because it

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requires measurements of $\phi$ in certain ranges of concentration which are often not attainable.

Indirect methods have also been applied for studying self-quenching which consist in following a competitive process, such as reaction or energy transfer, in which the excited molecule is involved [3, 9 - 11].

In this paper we describe an alternative approach to the study of self-quenching which requires measurements of emission intensity at a fixed wavelength as a function of concentration. This approach necessitates the use of a spectrofluorometer only and it is therefore very simple and easily handled.

The light absorbed by M at a certain wavelength varies with the concentration, following the exponential law

$$I_a = I_0\{1 - \exp(-2.3\epsilon l[\mathrm{M}])\} \tag{3}$$

where $\epsilon$ is the extinction coefficient. The intensity of the emitted light is proportional to the concentration of the excited state molecules:

$$[\mathrm{M}^*] = \frac{I_a \tau_\infty}{1 + k_{\mathrm{sq}}\tau_\infty[\mathrm{M}]} \tag{4}$$

as obtained by use of the steady state approximation in Scheme 1. Thus the following relationship can be obtained between the emitted light intensity $I$ and the concentration [M]:

$$I = K\,\frac{1 - \exp(-2.3\epsilon l[\mathrm{M}])}{1 + k_{\mathrm{sq}}\tau_\infty[\mathrm{M}]} \tag{5}$$

where $K$ is a constant that includes the exciting-light intensity, the radiative rate constant $k_r$ and the quantum yield and lifetime of the excited state. Equation (5) represents the ratio of two increasing functions of [M]. Therefore, the variation in $I$ with [M] shows a maximum corresponding to the value of [M] for which the following equality holds:

$$2.3\epsilon l(1 + k_{\mathrm{sq}}\tau_\infty[\mathrm{M}])\exp(-2.3\epsilon l[\mathrm{M}]) = k_{\mathrm{sq}}\tau_\infty\{1 - \exp(-2.3\epsilon l[\mathrm{M}])\} \tag{6}$$

Despite its complexity, eqn. (5) can be utilized for studying self-quenching in two limiting cases, in both of which the relationship between the emitted light intensity and the concentration becomes linear.

At high concentrations of M the exciting wavelength can be chosen in such a way that the absorbance ($\epsilon l$[M]) is sufficiently large to make the exponential term in eqn. (5) negligible. For such conditions, and taking eqn. (5) in its reciprocal form, one obtains

$$\frac{1}{I} = \frac{1}{K}(1 + k_{\mathrm{sq}}\tau_\infty[\mathrm{M}]) \tag{7}$$

A plot of $I^{-1}$ against [M] should be linear and the ratio of the slope to the intercept yields $k_{\mathrm{sq}}\tau_\infty$. This equation has been used by Vesley [12] to determine the self-quenching constant of $p$-hydroquinone in water and deuterium oxide from measurements of the fluorescence intensity as a function of concentration.

When the exciting wavelength is chosen so as to ensure a very low absorbance, the exponential function in eqn. (5) can be well approximated by limiting the Taylor expansion to

$$\exp(-2.3\epsilon l[\mathrm{M}]) \approx 1 - 2.3\epsilon l[\mathrm{M}] \tag{8}$$

This procedure changes the reciprocal of eqn. (5) into a linear function of the emitted light intensity with concentration:

$$\frac{1}{I} = K'([\mathrm{M}]^{-1} + k_{\mathrm{sq}}\tau_\infty) \tag{9}$$

where $K'$ is equal to $(2.3\epsilon lK)^{-1}$. The ratio of the intercept to the slope of the linear plot of $I^{-1}$ against $[\mathrm{M}]^{-1}$ yields $k_{\mathrm{sq}}\tau_\infty$.

Equation (9) can be applied to dilute as well as to concentrated solutions by using suitable exciting wavelengths. This method is free of the inconvenience of emission measurements in total absorption conditions (as needed for the application of eqn. (7)) and the experimental procedure is very simple and does not require sophisticated apparatus. Equation (9) was checked for some triplet sensitizers in which self-quenching may compete with energy transfer. The non-linear (eqn. (5)) and linear (eqn. (9)) fits of steady state emission data for 3-benzoylpyridine at two pH values are shown in Figs. 1 and 2. The maximum cannot be attained here because of the limited solubility of 3-benzoylpyridine in water; however, it can be estimated to occur at $[\mathrm{M}] = 1.4 \times 10^{-3}$ M at pH 9 and at $[\mathrm{M}] = 3.1 \times 10^{-3}$ M at pH 4.5. The shorter the lifetime is, the larger is the concentration required for the maximum to be observed. The results obtained are reported in Table 1 and compared, where possible, with those obtained by different methods.

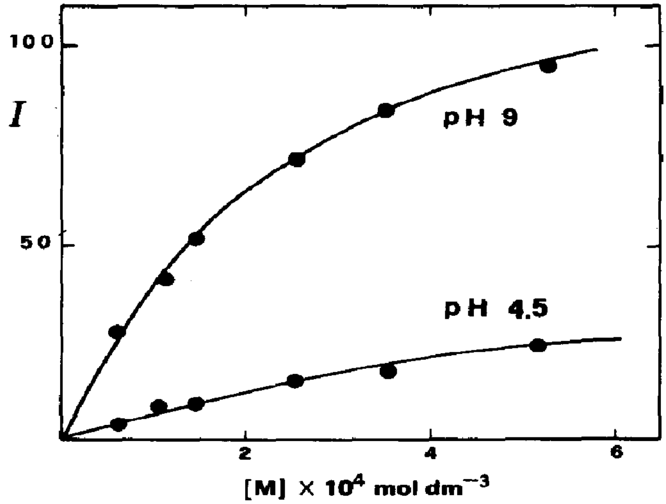

Fig. 1. Non-linear fit (eqn. (5)) of the emission intensities ($\lambda_{\mathrm{em}} = 460$ nm) of 3-benzoylpyridine ($\lambda_{\mathrm{exc}} = 330$ nm; calculated half-cell absorbance, 0.006 - 0.06).

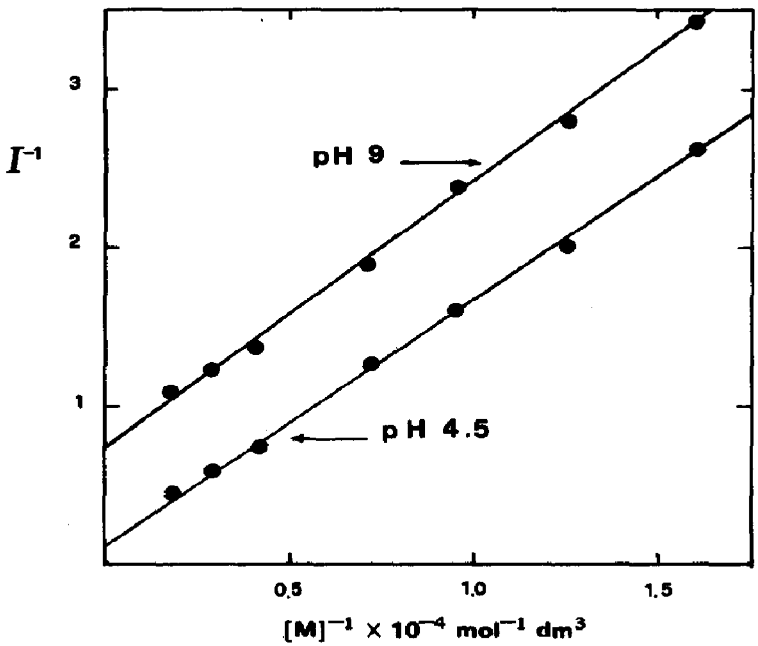

Fig. 2. Data of Fig. 1 treated according to eqn. (9).

It must be noted that self-quenching processes are of particular importance in the triplet state, because of the triplet's fairly long lifetime. Among the values in Table 1, for instance, the rate constant for $Ru(bpy)_3^{2+}$ (bpy ≡ 2,2′-bipyridine) has never been determined, despite the large number of

TABLE 1

Self-quenching data obtained by steady state emission measurements according to eqn. (9)

| *Compound (solvent)* | Intercept/slope ($\times 10^{-3}$ $M^{-1}$) | $\tau_\infty$ ($\mu s$) | $k_{sq}$ ($\times 10^{-8}$ $M^{-1}$ $s^{-1}$) | |
|---|---|---|---|---|
| Benzophenone (water, pH 7.4) | 25.4 | 215[a] | 1.2 | (1.6[a], 1.8[b]) |
| Benzophenone (water, pH 5.4) | 18.5 | 140[a] | 1.3 | (1.1[a]) |
| Benzophenone (water, pH 4.0) | 2.8 | 28[a] | 1.0 | (Not observed) |
| Benzophenone (water, pH 3.5) | 1.3 | 9.6[a] | 1.3 | (Not observed) |
| Benzoylpyridine (water, pH 9.0) | 3.9 | 69[c] | 0.56 | (0.55[c]) |
| Benzoylpyridine (water, pH 4.5) | 0.64 | 7.7[c] | 0.83 | (0.74[c]) |
| $Ru(bpy)_3^{2+}$ (water, air equilibrated) | 7.6 | 0.4[d] | 190 | (Not observed) |
| $Ru(bpy)_3^{2+}$ (water, deaerated) | 11.4 | 0.7[d] | 160 | (Not observed) |

The $k_{sq}$ values in parentheses refer to literature values obtained from different experiments.

[a] Data from ref. 9.

[b] Data from ref. 4.

[c] Data from ref. 8.

[d] Data from ref. 13. These data refer to dilute solutions, but not to infinitely dilute solutions, so therefore the corresponding $k_{sq}$ may be overestimated.

studies on this compound, because the process is hardly observable, owing to the short lifetime of the excited state at the concentrations generally used ($10^{-4}$ - $10^{-5}$ M). The sensitivity of the method is demonstrated also from the measurements on benzophenone in acidic solutions, where the low intensity of the emission does not allow lifetime measurements to be performed.

In conclusion, this method, which has only minimal equipment requirements, would appear to give reliable results and to be a useful alternative to more sophisticated procedures.

1 M. W. Wolf, K. D. Legg, R. E. Brown, L. A. Singer and J. P. Parks, *J. Am. Chem. Soc.*, *97* (1975) 4490.
2 M. W. Wolf, R. E. Brown and L. A. Singer, *J. Am. Chem. Soc.*, *99* (1977) 526.
3 D. I. Schuster and T. M. Weil, *J. Am. Chem. Soc.*, *95* (1973) 4091.
4 M. B. Ledger and G. Porter, *J. Chem. Soc., Faraday Trans. I*, *3* (1972) 539.
5 D. I. Schuster and M. D. Goldstein, *J. Am. Chem. Soc.*, *95* (1973) 986.
6 L. A. Singer, R. E. Brown and G. A. Davis, *J. Am. Chem. Soc.*, *95* (1973) 8638.
7 D. I. Schuster, M. G. Goldstein and P. Bane, *J. Am. Chem. Soc.*, *99* (1977) 187.
8 G. Favaro and F. Masetti, *J. Phys. Chem.*, *82* (1978) 1213.
9 G. Favaro and G. Bufalini, *J. Phys. Chem.*, *80* (1976) 800.
10 G. Favaro, *J. Photochem.*, *6* (1976/77) 139.
11 G. Favaro, *Chem. Phys. Lett.*, *23* (1973) 592.
12 G. F. Vesley, *J. Phys. Chem.*, *75* (1971) 1775.
13 F. Bolletta, M. Maestri and V. Balzani, *J. Am. Chem. Soc.*, *93* (1971) 1800.