Re-evaluation of the steady-state self-quenching constant of quinine bisulphate from fluorescence measurements in transmission geometry

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Abstract

In the present work we show that a recent methodology developed by us to acquire emission spectra and fluorescence quantum yields of highly absorbing samples in transmission configuration, constitutes a very simple and robust alternative to determine self-quenching constants, $K_{SQ}$. We measured the absorption and the steady-state emission spectra of quinine bisulphate, QBS, solutions ranging between $1.5 \times 10^{-3}$ and $1.5 \times 10^{-1}$ M. From these data, we calculated the expected emission spectra, affected by re-absorption, for all QBS concentrations. For higher concentrations, the re-absorption in the excitation/detection direction reaches values up to 6% of the total emitted intensity. The $K_{SQ}$ of the dye was re-evaluated from the concentration dependence of the quotients between the calculated and the experimental integrated emission spectra. The obtained value, $K_{SQ} = 18.4 \pm 0.1$ M$^{-1}$, shows no significant differences with those obtained from steady-state and average lifetimes by other authors, pointing out the diffusional nature of the self-quenching phenomenon. The present work helps clarify some ambiguous aspects concerning the photophysics of QBS, stressing that re-absorption phenomena must be considered in QBS concentrated solutions for accuracy measurements.

Introduction

Quinine bisulphate (QBS) is commonly used as a fluorescence quantum yield standard due to its following photophysical properties: (a) it shows no significant quenching by dissolved air, (b) it has a relatively high fluorescence quantum yield, $\Phi_F$, at infinite dilution and, (c) its absorption and fluorescence spectra exhibit a small overlap, preventing large re-absorption events. As a disadvantage, however, its fluorescence quantum yield decreases at higher concentrations due to the self-quenching phenomenon [1].

The importance of QBS as a fluorescence standard has been extensively reviewed by many authors, and different $\Phi_F$ values were reported using complementary experimental techniques [2–5]. One of the most referred values, 0.546, is the one originally reported by Melhuish [6] from the absolute Vavilov’s method. The calculation of this value involves extrapolation of the Stern–Volmer plot (with a steady-state self-quenching constant, $K_{SQ} = 15.0$ M$^{-1}$) at infinite dilution. More recently, Suzuki et al [7] have carried out a re-evaluation of $\Phi_F$ and $K_{SQ}$ values using an integrating sphere based method. The authors reported $\Phi_F = 0.60 \pm 0.02$ for $1 \times 10^{-5}$ M of QBS in 0.5 M of aqueous H$_2$SO$_4$ and $K_{SQ} = 28.5$ M$^{-1}$. The magnitude of the discrepancy between $\Phi_F$ values at diluted solutions is not acceptable for a reference material and underlines the necessity of a clear identification of the causes. In principle, the gap was assigned to differences in the self-quenching constants so, it looks like mandatory to have a reliable $K_{SQ}$ value, in order to accurately extrapolate $\Phi_F$ at infinite dilution.

The determination of $K_{SQ}$ from steady-state luminescence often requires measurements on samples...
with high solute concentrations. Generally, they are associated to high optical densities at the excitation and the emission wavelengths. The acquisition of emission spectra and $\Phi_F$ in these conditions is not a simple task due to the presence of inner-filter events \[8\]. As such, the consideration of these effects in the calculations is indispensable because, in this regime, the emitted light intensity is not proportional to the absorption factor. Consequently, the lack of consideration of these phenomena may induce serious misinterpretations of experimental data \[9, 10\].

In the past, the front-face configuration was the preferred geometry to determine $K_{SQ}$ \[6, 11, 12\]. However, this arrangement has the disadvantage that the penetration of the excitation light into the sample depends on the absorbance at the excitation wavelength, making the excitation volume different for different sample concentrations \[13\]. Moreover, the front-face measurements are often extremely sensitive to small changes in the incidence and the detection angles, which make them difficult to be performed in a commercial spectrophotometer.

In a recent work, we reported a simplified procedure to acquire emission spectra and $\Phi_F$ values of highly absorbing samples. The experimental setup consists in a commercial spectrophotometer adapted to transmission geometry, in which the detection of the emitted light is achieved at 180° with respect to the excitation beam. The main goal of this approach consists in the use of small optical path-lengths. In these cases, the small excitation and collection volumes overlap, and the differences between the spatial excitation and detection efficiencies inside the cell become irrelevant, independently of the absorption coefficient of the sample. The method also includes spectral and $\Phi_F$ corrections by means of a simplified mathematical approach that considers re-absorption events \[14\].

There are many examples in the literature that have analysed re-absorption and reemission phenomena. For example, Berberan Santos et al \[15\] have developed a complete stochastic theory that describes the molecular radiative transport of the exciting light. This stochastic theory — later extended to radiative and nonradiative transports \[16\] — leads to complex mathematical expressions, even for very simple geometries \[15\]. For this reason, Monte Carlo simulations are required for performing full numerical calculations, attending to the probabilistic nature of the radiative transport \[17\].

The method presented here avoids complex calculations because only a re-absorption step must be considered due to the geometrical arrangement at which the measurements were performed. As an advantage, compared with front-face and 90° conventional measurements, the technique avoids primary inner-filter effects.

In the present work we will show that our methodology represents a very simple and robust alternative to obtain steady-state self-quenching constants. As an illustrative example, we measured the absorption and the steady-state emission spectra of QBS solutions ranging between $1.5 \times 10^{-5}$ and $1.5 \times 10^{-1}$ M. From these data we calculated the expected emission spectra, affected by re-absorption, for all QBS concentrations. The $K_{SQ}$ of the dye was re-evaluated from the concentration dependence of the quotients between the calculated and the experimental integrated emission spectra. We will show the effect that causes the lack of re-absorption correction on the calculation of $K_{SQ}$, in order to discuss the differences observed with the previous reported values. Moreover, a discussion about the dynamic nature of the QBS self-quenching is also presented.

**Experimental section**

**Chemicals**

QBS (analytical reagent, purity > 99%) was purchased from Fluka and used as received. Acidic aqueous solutions of QBS, in a concentration range from $1.52 \times 10^{-5}$ to $1.52 \times 10^{-1}$ M, were prepared by dissolving the reagent in H$_2$SO$_4$ 0.5 M (Merck, 95%–97%, for analysis). Solutions were prepared with de-ionised water obtained from a Milli-Q system (18 MΩ × cm), and were left in the dark for one night before use.

Figure 1 shows the normalised absorption and emission spectra of a QBS solution of $1.52 \times 10^{-4}$ M, together with the transmission spectra of the optical filters used in the experiments (see below). QBS shows an absorption maximum at 347 nm ($\varepsilon = 5.41 \times 10^{4}$ M$^{-1}$ cm$^{-1}$) and an emission maximum at 454 nm \[18\].

**Measurements**

Absorption measurements were performed in a Cary 50 Conc UV–vis Spectrophotometer (Varian), equipped with a thermostated sample-holder. The bandwidth of the excitation slit was 1.5 nm.

![Figure 1. Normalised: (a) absorption (black line) and emission (red line) spectra of QBS in H$_2$SO$_4$ 0.5 M. Transmission spectra of Schott UG11 (dashed grey line) and WG360 (dashed orange line) optical filters.](image-url)
Steady-state fluorescence spectra were recorded in a Felix X32 PTI fluorometer, equipped with a xenon short-arc lamp UXL-75XE and a thermostated sample holder. The excitation and emission monochromators show gratings of 1200 line mm⁻¹, in which 1 mm correspond to a bandwidth of 4 nm. The excitation and emission slits were adjusted in all experiments to 0.375 mm, which is equivalent to a bandwidth of 1.5 nm. The choice of this bandwidth—similar to the one used in the absorption experiments—avoids distortions in the Lambert–Beer law [19].

The commercial spectrofluorometer was slightly modified in order to collect the emission at 180° with respect to the excitation beam (transmission configuration). A Schott UG11 filter (2 mm thickness) was intercalated between the excitation source and the sample, avoiding that some spurious excitation light of long wavelengths may reach the sample. In addition, the incorporation of a Schott WG360 filter (2 mm thickness) between the sample and the detector prevents the monochromatic excitation beam to reach the detector. A quartz cell of 0.2 cm path length was used for both, the absorption and the emission measurements. All measurements were performed at 20.0 ± 0.1 °C. A scheme of the experimental setup is shown in figure 2.

The ratio between the experimentally observed fluorescence quantum yields in the x direction, corresponding to concentrations \( C_0 \) and \( C \), \( \Phi_{\text{fl}}^{\text{obs}}(C_0)/\Phi_{\text{fl}}^{\text{obs}}(C) \), can be expressed as:

\[
\Phi_{\text{fl}}^{\text{obs}}(C_0) = f_x(\lambda_0, C) : \int_\lambda \Phi_{p,x}^{\text{obs}}(\lambda_0, \lambda, C_0) d\lambda = f_x(\lambda_0, C_0) : \int_\lambda \Phi_{p,x}^{\text{obs}}(\lambda_0, \lambda, C_0) d\lambda,
\]

where \( \Phi_{p,x}^{\text{obs}}(\lambda_0, \lambda, C) \) and \( \Phi_{p,x}^{\text{obs}}(\lambda_0, \lambda, C_0) \) represent the observed spectral photon irradiances in the x direction, at a fixed excitation wavelength, \( \lambda_0 \), for concentrations \( C_0 \) and \( C \), respectively. In equation (1), \( f_x(\lambda_0, C) \) and \( f_x(\lambda_0, C_0) \) symbolise the absorption factors, namely:

\[
f_x(\lambda_0, C) = (1 - 10^{-\text{A}(\lambda_0, C)}) \]

\[
f_x(\lambda_0, C_0) = (1 - 10^{-\text{A}(\lambda_0, C_0)})
\]

where \( \text{A}(\lambda_0, C) = \varepsilon(\lambda_0) \cdot C \cdot D \) and \( \text{A}(\lambda_0, C_0) = \varepsilon(\lambda_0) \cdot C_0 \cdot D \). In the last expressions, \( \varepsilon(\lambda_0) \) represents the molar absorption coefficient of the dye at \( \lambda_0 \) and \( D \) the optical path length.

The calculation of the emission spectra affected by re-absorption, \( \Phi_{p,x}^{\text{DRM}}(\lambda_0, \lambda, C) \), was performed using the differential re-absorption model, DRM [14], as follows: (a) an experimental emission spectrum from a dilute sample of concentration \( C_0 \), \( \Phi_{p,x}^{\text{obs}}(\lambda_0, \lambda, C_0) \), was selected; (b) this spectrum was divided by \( f_x(\lambda_0, C_0) \) and multiplied by \( f_x(\lambda_0, C) \) in order to obtain the calculated spectral photon irradiances in the x direction, \( \Phi_{p,x}^{\text{DRM}}(\lambda_0, \lambda, C) \), for the entire concentration range; (c) each \( \Phi_{p,x}^{\text{DRM}}(\lambda_0, \lambda, C) \) was then multiplied by \( \gamma_x^{\text{DRM}}(\lambda_0, \lambda, C) \) to obtain \( \Phi_{p,x}^{\text{DRM}}(\lambda_0, \lambda, C) \), where \( \gamma_x^{\text{DRM}}(\lambda_0, \lambda, C) \) is a factor that relates the emission spectrum affected by re-absorption with the unaffected one, namely [14]:

\[
\gamma_x^{\text{DRM}}(\lambda_0, \lambda, C) = \frac{\text{A}(\lambda_0, C)}{\text{A}(\lambda_0, C) - \text{A}(\lambda, C)} \frac{(1 - 10^{-\text{A}(\lambda_0, C)})}{(1 - 10^{-\text{A}(\lambda_0, C_0)})}.
\]

The ratio of interest can now be obtained as:

\[
\frac{\Phi_{\text{fl}}^{\text{obs}}(C)}{\Phi_{\text{fl}}^{\text{obs}}(C_0)} = \frac{\int_\lambda \Phi_{p,x}^{\text{obs}}(\lambda_0, \lambda, C) d\lambda}{\int_\lambda \Phi_{p,x}^{\text{obs}}(\lambda_0, \lambda, C_0) d\lambda},
\]

where the integrals must be performed over the entire range of emission wavelengths.

In the same context, our model also allows the calculation of \( p_x^{\text{DRM}} \), the mean probability of re-absorption in the x direction integrated over the emission spectrum, defined as [14]:
Concentration values higher than 1.52 × 10⁻³ M are accompanied by changes at the red edge. This feature is not observed in figure 5, indicating that the re-emitted light is actually not detected. 

\[ L_{p,x}(\lambda_0, \lambda, C) \] and \[ L_{p,x}^{\text{DRM}}(\lambda_0, \lambda, C) \] were computed as described in the experimental section, using the QBS solution of 1.52 × 10⁻³ M as \( C_0 \). This concentration represents the highest one for which self-quenching can be considered negligible. Moreover \( L_{p,x}^{\text{DRM}} = 0.001 \) is less than the proposed 0.02 lower limit [14] below which re-absorption effects should be considered.

Figure 6 compares \( L_{p,x}(\lambda_0, \lambda, C) \), \( L_{p,x}^{\text{DRM}}(\lambda_0, \lambda, C) \) and \( L_{p,x}^{\text{obs}}(\lambda_0, \lambda, C) \) for four QBS concentrations. The three spectra coincide for 3.04 × 10⁻³ M (figure 6(a)), a value sufficiently low to disregard re-absorption and self-quenching effects. For a QBS concentration of 3.04 × 10⁻³ M, the re-absorption remains unimportant, whereas self-quenching begins to be appreciable (figure 6(b)). For concentrations of the order of, or higher than 3.04 × 10⁻² M, the re-absorption starts to be significant, as can be seen in figures 6(c) and (d). Moreover, the similarities observed between the spectral shapes of the normalised \( L_{p,x}^{\text{DRM}}(\lambda_0, \lambda, C) \) and \( L_{p,x}^{\text{obs}}(\lambda_0, \lambda, C) \) (data not shown), ensures the absence of other emitting species.

Figure 7 shows \( \Phi_{F,x}^{\text{DRM}}(C)/\Phi_{F,x}^{\text{obs}}(C) \), calculated from equation (4), as a function of QBS concentration. The slope of the Stern–Volmer plot using these data yields \( K_{SQ} = 18.4 \pm 0.1 \text{ M}^{-1} \). On the other hand, the plot of \( \Phi_{F,x}^{\text{obs}}(C_0)/\Phi_{F,x}^{\text{obs}}(C) \) versus QBS concentration, neglecting re-absorption events, yields \( K_{SQ} = 19.9 \pm 0.2 \text{ M}^{-1} \). Clearly, the decrease of the intensity observed at the blue edge of the spectra due to re-absorption, although small, causes a significant increment in the Stern–Volmer slope, leading to an over-estimation in the \( K_{SQ} \) value. Table 1 summarises the most relevant photophysical parameters for QBS obtained in this work.

Our self-quenching constant value of 18.4 M⁻¹ is similar to the one reported by Melhuish (\( K_{SQ} = 15.0 \text{ M}^{-1} \)) [8]. Contrasting, the more recent value reported by Suzuki et al (\( K_{SQ} = 28.5 \text{ M}^{-1} \))[7] is ~50% larger. As a plausible reason to account for this discrepancy one could invoke the absence of any treatment of effect originated in re-absorption phenomenon.

In previous paragraph we have shown that over-estimated \( K_{SQ} \) values can be obtained if re-absorption effects are not considered. Suzuki et al have used QBS concentrations as large as 7 × 10⁻³ M in a 1 × 1 cm optical cell, which is located inside an integrating sphere. Using equations (3) and (5), a simple calculation yields a non negligible ~3% re-absorption probability for this sample in transmission geometry. Note that re-absorption effects can be greatly enhanced inside the integrating sphere due to multiple internal reflections. Although the authors carefully considered re-absorption and re-emission corrections in the optical irradiation were re-emitted and further collected, the changes at the blue edge of the spectra should be accompanied by changes at the red edge. This feature would not be detected.

\[
P_{0,x}^{\text{DRM}}(\lambda_0, C) = \int L_p(\lambda) \cdot [1 - \gamma_{x}^{\text{DRM}}(\lambda_0, \lambda, C)] \, d\lambda,
\]

where \( L_p(\lambda) \) is the normalised, to unit area, fluorescence spectrum.

**Results and discussion**

Figure 3 shows \( f_x(\lambda_0, C) \) for QBS samples ranging between 1.52 × 10⁻⁵ and 1.52 × 10⁻¹ M. For concentration values higher than 1.52 × 10⁻³ M, the amount of absorbed light at 345 nm reaches unity, indicating the total absorption of the excitation beam along an optical path-length of 0.2 cm.

The fluorescence spectra of the same set of solutions, recorded at \( \lambda_0 = 345 \text{ nm} \), are shown in figure 4. For concentration values lower than 1.52 × 10⁻³ M, the emission intensity increases with \( f_x(\lambda_0, C) \). On the other hand, for concentration values higher than 1.52 × 10⁻³ M, the emission intensity decreases, being \( f_x(\lambda_0, C) \approx 1 \). The loss of fluorescence intensity observed in concentrated solutions is due to a concentration self-quenching phenomenon, which leads to a decrease in the emission intensity without changes in the spectrum shape.

In order to verify if the fluorescence spectra present changes in their shape, normalised emission spectra of QBS solutions are plotted in figure 5. For concentration values higher than 1.52 × 10⁻² M, the spectral shape changes in the region between 375 and 430 nm (at the overlap region between absorption and emission spectra) and can be assigned to re-absorption. In principle, the large Stokes-shift and the \( \Phi_x \) value of QBS prevent the existence of re-absorption and re-emission events. In our experiments, only a small re-absorption at highly concentrated solutions is observed. It is interesting to note that, if the re-absorbed radiation were re-emitted and further collected, the changes at the blue edge of the spectra should be accompanied by changes at the red edge. This feature would not be detected.
determination of $\Phi$ values for anthracene and 9,10-diphenylanthracene, they did not mention any correction for QBS samples. As such we tend to believe that the absence of any consideration of these phenomena could be the cause of the observed discrepancy in the $K_{SQ}$ values.

Different authors have reported unusual non-exponential decays along the entire emission spectrum for QBS [20–22]. The decays at different $\lambda_{em}$ have been usually fitted by bi-exponential functions, and a negative coefficient was necessary to adjust the data at $\lambda_{em} > 450$ nm due to the presence of a characteristic rise-time. Moreover, the time-resolved emission spectra also show a remarkable red-shift in fluid solution at room temperature. These results, in addition to those obtained from the emission and the excitation anisotropy experiments [23], strongly suggest the existence of more than one emitting state. Despite the variety of available results [24–28], the complex photophysical behaviour of QBS still remains not fully clarified.

Since emission spectrum is not originated from a single excited state, the only magnitude of interest is the quenching of the total emission spectrum. In the case of complex emission decays, the average decay times are proportional to the steady-state intensity [29]. Mishra et al [28] have reported the decrease of the average decay times of QBS when the concentration of the dye increases from $10^{-5}$ to $10^{-1}$ M. From these data one can obtain $K_{SQ} = 19$ M$^{-1}$, which is in total agreement with the results obtained in the present work suggesting the diffusional nature of the QBS self-quenching phenomenon.

Conclusions

We have shown that the recent methodology developed by us to acquire emission spectra and $\Phi_F$ of highly absorbing samples is adequate to determine $K_{SQ}$ in samples with a single absorbing and emitting compound.

In principle, the large Stokes-shift and the $\Phi_F$ value of QBS should prevent the existence of re-absorption and re-emission events. However, in our experiments, the re-absorption in the excitation/detection direction reaches values up to 6% of the total emitted intensity. Although re-absorption is significant, the re-emission remains undetectable for the geometric reasons described in our previous work [14]. The presence of re-absorption events confirms that it is necessary to perform appropriated corrections on emission spectra for the accurate data processing. The calculation using emission spectra after re-absorption corrections yields $K_{SQ} = 18.4 \pm 0.1$ M$^{-1}$, showing no significant differences with those obtained from steady-state [6] and average lifetimes [28] by other authors.

The $K_{SQ}$ value determined in this work points out that the extrapolation at infinite dilution performed by Melhuish is not the reason that justifies $\Phi_F$ values lower than those reported by Suzuki et al. Moreover, we have shown that re-absorption in QBS concentrated solutions is not negligible, a fact that must be taken into account for accuracy measurements. Since re-absorption is present, the measurements with an integrating sphere could be affected by reemission, a fact that could cause upper $\Phi_F$ values that those expected.
The present work helps clarify some ambiguous aspects concerning the photophysics of QBS, whereas the complete photophysical characterisation of the dye needs more effort in the future.

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Table 1. Experimental and calculated photophysical parameters of QBS in H$_2$SO$_4$ 0.5 M.

| (QBS) M$^{-1}$ | $\Phi_{F_{C_x}}^{\text{DRM}}(C)$ | $\Phi_{F_{C_x}}^{\text{obs}}(C)$ | $\Phi_{F_{C_x}}^{\text{obs}}(C_0)$ | $p_{\text{DRM}}^{\text{obs}}$ |
|--------------|-------------------|-------------------|-------------------|-------------------|
| 1.52 $\times$ 10$^{-5}$ | 0.99 | 0.99 | 0.001 | 0.001 |
| 3.04 $\times$ 10$^{-5}$ | 1.00 | 1.00 | 0.001 | 0.001 |
| 5.06 $\times$ 10$^{-5}$ | 1.01 | 1.01 | 0.001 | 0.001 |
| 8.10 $\times$ 10$^{-5}$ | 1.00 | 1.00 | 0.001 | 0.001 |
| 1.52 $\times$ 10$^{-4}$ | 1.00 | 1.00 | 0.001 | 0.001 |
| 3.04 $\times$ 10$^{-4}$ | 1.01 | 1.01 | 0.002 | 0.002 |
| 5.06 $\times$ 10$^{-4}$ | 1.02 | 1.02 | 0.002 | 0.002 |
| 8.10 $\times$ 10$^{-4}$ | 1.04 | 1.04 | 0.002 | 0.002 |
| 1.52 $\times$ 10$^{-3}$ | 1.05 | 1.06 | 0.003 | 0.003 |
| 3.04 $\times$ 10$^{-3}$ | 1.08 | 1.08 | 0.005 | 0.005 |
| 5.06 $\times$ 10$^{-3}$ | 1.11 | 1.12 | 0.008 | 0.008 |
| 8.10 $\times$ 10$^{-3}$ | 1.17 | 1.17 | 0.007 | 0.007 |
| 1.52 $\times$ 10$^{-2}$ | 1.29 | 1.31 | 0.017 | 0.017 |
| 3.04 $\times$ 10$^{-2}$ | 1.53 | 1.57 | 0.024 | 0.024 |
| 5.06 $\times$ 10$^{-2}$ | 1.89 | 1.95 | 0.032 | 0.032 |
| 8.10 $\times$ 10$^{-2}$ | 2.45 | 2.56 | 0.045 | 0.045 |
| 1.52 $\times$ 10$^{-1}$ | 3.77 | 4.02 | 0.061 | 0.061 |

Molar QBS concentration, (QBS); integrated fluorescence quantum yield quotients considering DRM in the x direction for $C$, $\Phi_{F_{C_x}}^{\text{DRM}}(C)/\Phi_{F_{C_x}}^{\text{obs}}(C)$; integrated experimentally observed fluorescence quantum yield quotients for $C_0$ and $C$ in the x direction, $\Phi_{F_{C_x}}^{\text{obs}}(C_0)/\Phi_{F_{C_x}}^{\text{obs}}(C)$; mean re-absorption probability in the x direction from the differential re-absorption model, $p_{\text{DRM}}^{\text{obs}}$.

Conflicting interests

The authors have declared that no conflicting interests exist.
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