

Letter to the Editor

# Chemical optical sensing based on luminescence lifetime measurements: *a caveat*

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## Abstract

Optical sensors based on the luminescence lifetime quenching are often considered as being more attractive than luminescence intensity-based sensors. However, depending on the nature of the luminophore–matrix system considered, the relative positions of the  $I_0/I$  and  $\tau_0/\tau$  curves as a function of the quencher concentration can vary considerably. With a view to rationalize these observations, numerical computations of the  $I_0/I$  and  $\tau_0/\tau$  ratios have been performed in a two-site model. It is shown that this simple model can explain the various observations and that lifetime measurements performed by phase fluorometry are sometimes not suitable for analytical application. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Optical sensors; Luminescence lifetime; Phase fluorometry; Stern–Volmer plot; Numerical computations.

## Introduction

Many chemical optical sensors are based either on luminescence intensities or on luminescence lifetimes, the latter usually measured by phase fluorometry. Benefits brought about by the latter technique have been stressed [1–3]: self-referencing, insensitivity to total signal level and fluctuations, and thus insensitivity to bleaching and leaching of the luminophore. However, in a critical review on luminescence decay-time-based optical sensors, Lip-pitsch and Draxler attracted attention to possible drawbacks of this approach [4].

When luminescence intensities are measured, one usually makes use of a Stern–Volmer (S–V) type plot to calibrate the sensor. The ratio of the light intensities ( $I_0/I$ ) in the absence and in the presence of the analyte (quencher) is given as a function of the analyte concentration. The graph is often downward curved. This feature is ascribed to microheterogeneities in the sensing phase [5]. Alternatively, if phase fluorometry is used at one angular modulation frequency  $\omega$ , variation of the *average* value of the lifetime  $\tau$  due to the presence of analyte is usually calculated using equation (1):

$$\tau = \omega^{-1} \tan \phi \quad (1)$$

where  $\phi$  is the measured phase shift. Although equation (1) is strictly applicable only to monoexponential decays, its use to calibrate sensors is quite acceptable. Here, also, the ratio  $\tau_0/\tau$  is presented as a function of the analyte concentration and the graph is again often downward curved.

Our attention was drawn to the following observation: depending on the nature of the sensing phase, the relative positions of the  $I_0/I$  and  $\tau_0/\tau$  curves vary considerably. For example,  $I_0/I > \tau_0/\tau$  for the luminophore tris(2,2'-bipyridine)ruthenium(II) dichloride adsorbed on kieselgel beads and embedded in silicone films, at all O<sub>2</sub> pressures (0–1 atm) [1]. The large difference between all the  $I_0/I$  and  $\tau_0/\tau$  measured values indicates that this observation cannot be the result of experimental uncertainties.

In contrast, for the same range of O<sub>2</sub> pressures, Camerman et al. [6,7] found that  $I_0/I < \tau_0/\tau$  for the sensor phase made of a tris(7,8-benzoquinoline)iridium(III) complex adsorbed on Amberlite® XAD4 and embedded in silicone films.

Also, Hartmann et al. [8] reported  $I_0/I$  ratios slightly larger than the corresponding  $\tau_0/\tau$  ratios in the low oxygen partial pressure region and the opposite behaviour at higher  $pO_2$  values. In this case, the sensing phase was tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) perchlorate dissolved in polystyrene [8].

## Aim and results

With a view to rationalize and perhaps to understand these various, apparently conflicting observations, we performed numerical computations of the  $I_0/I$  and  $\tau_0/\tau$  ratios under many different physically expected conditions. The most simple model that can satisfactorily mimic negative curvatures of S–V plots is the discrete two-site model. Perhaps a more realistic model is based on Gaussian distributions of the sites. Nevertheless it was felt that if a fairly simple model could rationalize the observed behaviours, a model with more adjustable parameters would also do it.

In the two-site model, the  $I_0/I$  and the  $\tau_0/\tau$  ratios are given by equations (2) and (3) respectively [4,5]:

$$I_0/I = 1 / \sum_{i=1}^2 \{f_i / (K_{SVi}[Q])\} \quad (2)$$

$$\tau_0/\tau = \frac{\sum_{i=1}^2 a_i \tau_{0i}^2 / (1 + \omega^2 \tau_{0i}^2)}{\sum_{i=1}^2 a_i \tau_{0i} / (1 + \omega^2 \tau_{0i}^2)} \times \frac{\sum_{i=1}^2 a_i \tau_i^2 / (1 + \omega^2 \tau_i^2)}{\sum_{i=1}^2 a_i \tau_i^2 / (1 + \omega^2 \tau_i^2)} \quad (3)$$

where the following notations have been used:  $f_i$ , fractions of total light emitted from each site in the absence of quencher;  $K_{SVi}$ , S–V constants for the two sites;  $[Q]$ , quencher concentration or partial pressure;  $\tau_{0i}$ , true lifetime of each site in the absence of quencher;  $\tau_i$ , true

lifetime of each site in the presence of quencher;  $a_i$ , signal amplitude of each site measured by phase fluorometry; and  $\omega$ , angular modulation frequency of the exciting light.

The parameters are linked by equations (4) and (5):

$$f_i = \int_0^{+\infty} a_i e^{-t/\tau_{0i}} dt \quad (4)$$

and

$$\tau_i = 1 / \{ \tau_{0i}^{-1} + k_{Qi}[Q] \} \quad (5)$$

where the  $k_{Qi}$ 's are the bimolecular quenching constants of the luminophore in each site. Thus  $K_{SVi} = k_{Qi} \tau_{0i}$ . Equation (2) can be simplified using equations (4) and (5):

$$I_0/I = 1 / \sum_{i=1}^2 a_i \tau_i \quad (6)$$

To perform the simulations, numerical values have to be assigned to the  $f_i$ 's and  $K_{SVi}$ 's. The following values were chosen:  $K_{SV1}$  ( $\text{atm}^{-1}$ ) = 0.49;  $K_{SV2}$  ( $\text{atm}^{-1}$ ) = 3.47;  $f_1 = 0.25$  and  $f_2 = 0.75$ . It was found during our experimental study of the luminescence quenching by  $\text{O}_2$  of tris(1,10-phenanthroline)ruthenium(II) dichloride embedded in a dip-coated sol-gel film [9] that the above-mentioned values gave the best fit between the experimental data and the calculated values (see the figure). Thus, the chosen parameter values correspond to a physically realistic situation. Nevertheless, the exact values given to the  $K_{SVi}$ 's are not critical. Indeed, computations performed with other sets of  $K_{SVi}$ 's led to the same conclusions. The frequency  $\nu$  was fixed at 100 kHz ( $\omega = 2\pi\nu$ ) which is

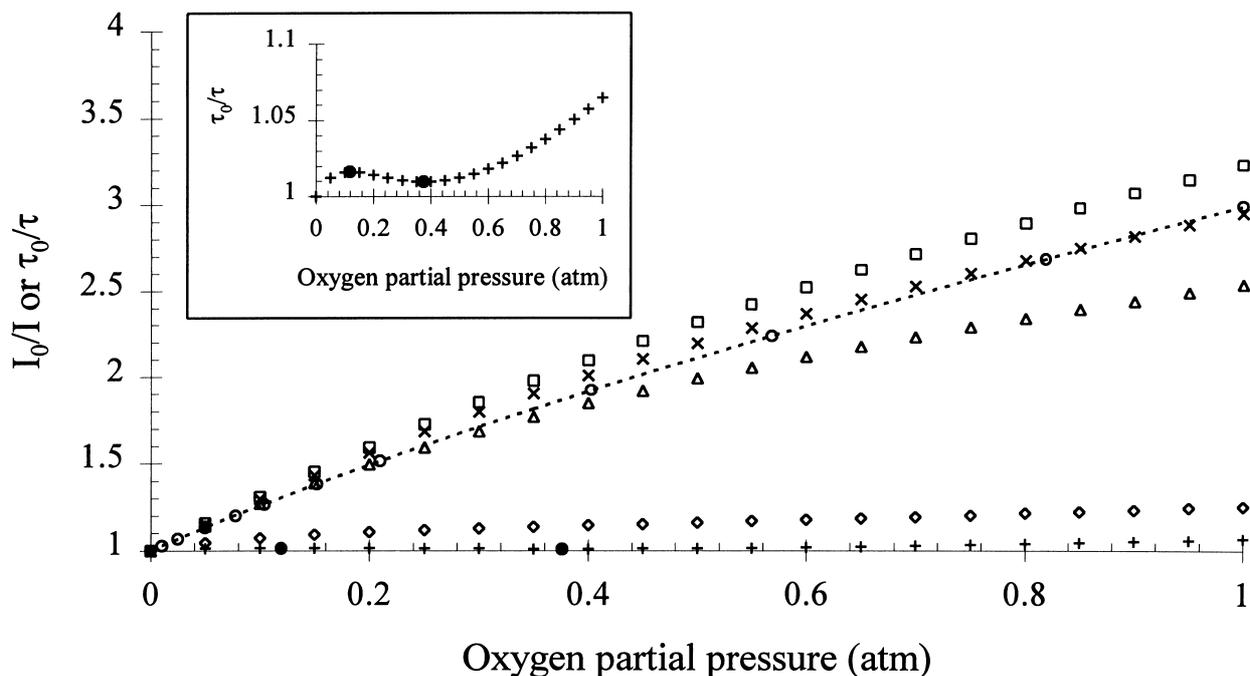


Fig. 1.  $I_0/I$  and  $\tau_0/\tau$  ratios versus oxygen partial pressure.  $I_0/I$ :  $\circ$  (experimental), --- (calculated);  $\tau_0/\tau$ :  $\tau_{01}$  is kept constant (0.425  $\mu\text{s}$ ), (1)  $\tau_{02} = 0.970$   $\mu\text{s}$ :  $\square$ ; (2)  $\tau_{02} = 0.760$   $\mu\text{s}$ :  $\times$ ; (3)  $\tau_{02} = 0.540$   $\mu\text{s}$ :  $\triangle$ ; (4)  $\tau_{02} = 0.200$   $\mu\text{s}$ :  $\diamond$ ; (5)  $\tau_{02} = 0.0755$   $\mu\text{s}$ :  $+$ . The two extrema are represented by  $\bullet$ . Insert: calculated  $\tau_0/\tau$  vs.  $p_{\text{O}_2}$  showing the positions of the maximum and the minimum values ( $\bullet$ ).

well below the region where  $\tau_0/\tau$  becomes frequency independent ( $\sim 4 \times 10^7$  Hz).

From the computations we performed, it was concluded that five typical cases can be selected (see the figure).

#### Case 1

$$\tau_{01} = 0.425 \mu\text{s} \text{ and } \tau_{02} = 0.970 \mu\text{s}$$

The strongly quenched site (largest  $K_{SV}$ ) has the longest lifetime. The  $\tau_0/\tau$  curve is at all quencher pressures above the  $I_0/I$  curve.

#### Case 2

$$\tau_{01} = 0.425 \mu\text{s} \text{ and } \tau_{02} = 0.760 \mu\text{s}.$$

Here the difference between the  $\tau_{0i}$ 's is smaller and the strongly quenched site still has the longest lifetime. The  $\tau_0/\tau$  curve lies above the  $I_0/I$  curve at low quencher pressures. However the two curves cross at a  $pO_2$  of ca. 0.85 atm.

#### Case 3

$$\tau_{01} = 0.425 \mu\text{s} \text{ and } \tau_{02} = 0.540 \mu\text{s}.$$

The two sites display similar lifetimes. The  $\tau_0/\tau$  curve now lies mainly below the  $I_0/I$  curve, the curves are identical in the region of low  $O_2$  pressures (ca.  $< 0.20$  atm).

#### Case 4

$$\tau_{01} = 0.425 \mu\text{s} \text{ and } \tau_{02} = 0.200 \mu\text{s}.$$

The strongly quenched site has the shortest lifetime. To our knowledge, this case has up to now never been observed and is thus not backed by experimental results. Yet, it is interesting to consider this situation (see especially case 5). The  $\tau_0/\tau$  curve is now totally below the  $I_0/I$  curve. The  $\tau_0/\tau$  ratio increases very slowly with the  $O_2$  partial pressure and tends to level off.

#### Case 5

$$\tau_{01} = 0.425 \mu\text{s} \text{ and } \tau_{02} = 0.0755 \mu\text{s}.$$

$\tau_{02}$  is smaller than in case 4. At all  $O_2$  pressures, one finds  $\tau_0/\tau < I_0/I$ . A maximum and a minimum in the  $\tau_0/\tau$  curve appear respectively at  $pO_2 \cong 0.1$  atm and  $pO_2 \cong 0.4$  atm.

The exact position of the extrema can be found by deriving equation (3) with respect to  $pO_2$ . This was done by symbolic computation with the help of the Mathematica 2.2<sup>®</sup> software and leads to equation (7):

$$d(\tau_0/\tau)/dpO_2 = \tau_0 \{ [(A+B)/C] - DE/C^2 \} \quad (7)$$

in which  $A, B, C, D, E$  are combinations of all the parameters defined in equations (2) and (3). After replacing the  $K_{SVi}$ 's,  $f_i$ 's and  $\tau_{0i}$ 's by their numerical values (case 5), a 14-root equation is obtained. Fortunately, using the same software it was found that only two roots are real and positive and thus physically acceptable. Details of the computations can be obtained on request or found on the Web site <http://www.ulb.ac.be/sciences/cop/>.

A maximum and a minimum in the  $\tau_0/\tau$  curve are indeed found for  $pO_2$  values of 0.12 atm and 0.38 atm, respectively. This is shown in the figure insert. Computations performed for frequencies of 50 and 200 kHz lead to qualitatively similar findings.

## Conclusion

Although lifetime-based sensing undoubtedly offers several advantages over light-intensity sensing, as discussed in the Introduction, there are cases where the lifetime measurements by phase fluorometry will not be suitable for analytical applications. This is so when the  $\tau_0/\tau$  curve levels off or displays extrema and would arise when a strongly quenched site has a short lifetime compensated by a large bimolecular quenching constant. Yet, this situation is up to now not backed by any experimental results.

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