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Erythrosin B encapsulated in a fluoropolymer matrix for dissolved oxygen optical sensing in aggressive aqueous environments

R.N. Gillanders, M.C. Tedford, P.J. Crilly, R.T. Bailey*

Department of Chemical and Biological Sciences, Bell College of Technology, Almada Street, Hamilton ML3 0JB, UK

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Abstract

A robust thin film dissolved oxygen sensor was fabricated by trapping erythrosin B in a flexible fluoropolymer matrix. Strong phosphorescence, which was partially quenched by dissolved oxygen, was observed when the sensor was immersed in water. Residual phosphorescence, which was not quenched by dissolved oxygen, was attributed to the presence of aggregated dye species. The sensor was optically transparent, resistant to contamination, with good mechanical properties. Fast response, coupled with good sensitivity and resistance to leaching, were also exhibited by this system. The Stern–Volmer (SV) plot exhibited marked downward turning at higher oxygen concentrations. A linear plot was obtained when the SV equation was modified to account for the varying sensitivity of dye molecules in the matrix to the quencher.

Keywords: Erythrosin B; Dissolved oxygen; Sensor; Fluoropolymer; Phosphorescence

1. Introduction

There is currently considerable demand for dissolved oxygen sensors which will operate for prolonged periods in hostile and corrosive environments such as those found in many chemical processes and effluent discharges. Conventional electrochemical (Clark cell) detectors are not suitable for such environments since they are easily poisoned. Consequently, considerable effort has been expended in the development of robust optical sensors based on oxygen sensitive dyes encapsulated in chemically resistant sol gels or polymers. Besides being inert, suitable matrices must be able to dissolve the dye, and be permeable to oxygen. They should also be impermeable to liquid water, and dissolved species such as metal ions, proteins, oxidants and reductants which interfere with the operation of the sensor.

Luminescent quenching of organic fluorophores can form the basis of dissolved oxygen detectors due to their fast response, high sensitivity and specificity [1–6]. Unlike electrochemical detectors, they are not easily poisoned. Most of these have been based on transition-metal complexes in polymer or sol–gel matrices and have been mainly used to measure gaseous oxygen [7–12].

Erythrosin B has been shown to be a suitable probe dye for the detection of both gaseous and dissolved oxygen. [13–18]. Previous studies have shown that in sol gel matrices, erythrosin phosphorescence is highly quenched by liquid water [18]. Erythrosin B doped sol gels have been evaluated as phosphorescent dissolved oxygen sensors, but only in the form of monoliths containing a relatively high concentration of dye to compensate for excited triplet quenching by water hydroxyl vibrations [17]. Recently, studies of erythrosin B/sol gel thin films found no detectable phosphorescence, but found weak fluorescence which was very efficiently quenched by dissolved oxygen. These results were explained on the basis of a singlet oxygen feedback mechanism [18].

In many respects, highly fluorinated polymers are ideal matrices for organic fluorophores. They are inert, permeable to oxygen and since they are hydrophobic offer protection from many charged species which may poison the dye. Unfortunately, many highly fluorinated organic polymers are insoluble in common solvents rendering them unsuitable for fabricating thin film sensors. One such polymer, which is inexpensive and commercially available, is a copolymer of tetrafluoroethylene, vinylidine fluoride and propylene. This is a colourless rubbery material soluble in ketones and esters. In this report, this polymer is investigated as a

* Corresponding author. Present address. Thomas Graham Building, Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, UK. Tel.: +44-141-548-2277; fax: +44-141-548-4822.
E-mail address: r.bailey@strath.ac.uk (R.T. Bailey).

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suitable host material for the probe dye erythrosin B, with a view to construct a sensitive, robust, dissolved oxygen sensor suitable for use in aggressive aqueous environments.

In a homogeneous solution when only dynamic quenching is present, the emission intensity of a lumophore which decays naturally by a first-order process, and which is quenched bimolecularly by oxygen (often at a diffusion controlled rate), is given by the Stern–Volmer (SV) equation:

$$\frac{I_0}{I} = 1 + \tau_0 k_q [O_2] \quad (1)$$

where I_0 is the emission intensity of a lumophore which decays naturally in the absence of oxygen, I the emission intensity in the presence of oxygen, τ_0 the lifetime of the fluorescing state in the absence of oxygen, and k_q the bimolecular rate constant for quenching by oxygen. The equivalent kinetic equation is

$$\frac{\tau_0}{\tau} = 1 + \tau_0 k_q [O_2] \quad (2)$$

where τ is the lifetime in the presence of oxygen concentration $[O_2]$. In both cases, the dynamic Stern–Volmer constant K_{SV} is $\tau_0 k_q$. The two equations are equivalent when no static quenching is involved.

Frequently, optical sensors based on matrix encapsulated luminescent dyes, deviate from the Stern–Volmer equation at higher oxygen concentrations. Usually, a downward turning curve is found, which is frequently attributed to dynamic quenching combined with a heterogeneous environment for the dye molecules. This behavior can generally be fitted by a two-site model [19]. An alternative model invokes both dynamic and static quenching and can predict a decay curve, which has a quadratic dependence on quencher concentration and turns upward at higher quencher concentration [19].

2. Experimental

2.1. Chemicals and materials

Erythrosin B (95% pure) were obtained from Aldrich and used as received. The fluorinated polymer an amorphous random copolymer of tetrafluoroethylene (~56 wt.%), vinylidine fluoride (~27 wt.%), and propylene (~17 wt.%) was obtained from Aldrich and used without further purification. Glass microscope slides were obtained from Fischer, and cut to dimensions 12 mm × 25 mm, were used as substrates for the sensor films. All other chemicals and solvents were reagent grade and used without further purification. De-ionized water was used throughout.

2.2. Procedures

An alkaline detergent wash, followed by immersion in a solution of ammonium persulphate in 98% sulphuric acid for at least 12 h at room temperature, cleaned the substrates. This was followed by thorough washing in room temperature de-ionized water, after which the slides were oven dried at 110 °C. The sensors were prepared by dip-coating or spin-coating on cleaned substrates using a 5% solution of the polymer in methyl ethyl ketone (MEK) containing erythrosin B at a concentration of 10^{-4} M. The film thickness was found to be about 3 μm on each side of the support for the dip-coated and 0.6 μm on one side only for the spin-coated films. The slides were dried at room temperature for several days or in a vacuum oven at room temperatures for at least 6 h. The final polymer coatings were optically transparent, rubbery but tough, and adhered well to the glass substrate. They were not affected by prolonged immersion in water. The UV-Vis absorption spectra were recorded using a Helios β UV-Vis spectrophotometer. Steady-state luminescence measurements were made using a Perkin-Elmer LS 45B fluorimeter with 530 nm excitation and 10 nm slit widths.

The coated slides were placed diagonally in a standard polymethylmethacrylate 1 cm × 1 cm cuvette and the phosphorescence collected at 90° to the exciting radiation beam.

Water samples containing different concentrations of dissolved oxygen were obtained by bubbling pure oxygen, air and argon slowly through distilled water, at room temperature for at least 15 min. Other oxygen intermediate dissolved oxygen concentrations were obtained by bubbling appropriate gas mixtures through the water until equilibrium was reached. Oxygen concentrations up to 20 mg l^{-1} (the limit of the meter) were checked using a calibrated Oakton dissolved oxygen meter.

3. Results and discussion

3.1. Luminescence emission

The structure of erythrosin B, a xanthene dye, is shown in Fig. 1 together with the structure of the fluoropolymer.

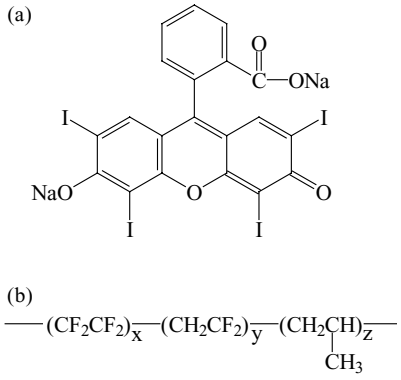

Fig. 1. (a) Structure of erythrosin B. (b) Structure of Fluoropolymer (x =~ 56 wt.%; y =~ 27 wt.%; z =~ 17 wt.%).

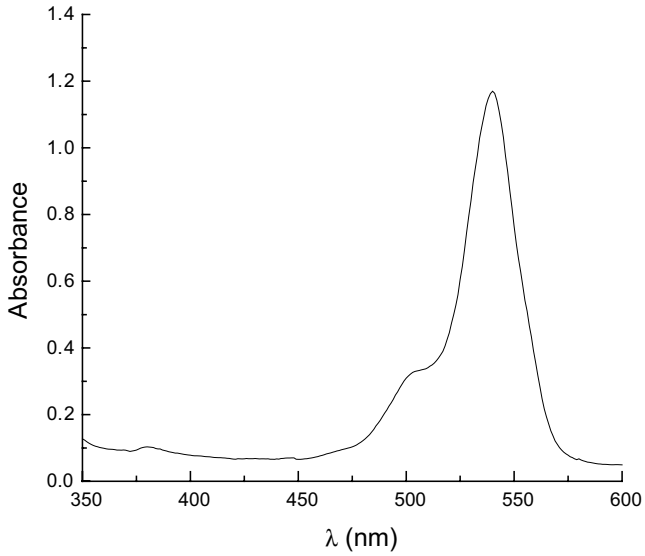

Fig. 2. Absorption spectrum of erythrosin B in methyl ethyl ketone solution.

The absorption spectrum of a solution of the dye in MEK is shown in Fig. 2. The absorption spectrum of a typical dip-coated slide is shown in Fig. 3. Both spectra show a strong, broad, absorption near 530 nm with a high frequency shoulder. The encapsulated dye absorption however, at 524 nm is blue shifted with respect to the solution absorption at 531 nm, and is also much broader. With excitation at 530 nm, strong phosphorescent emission at 680 nm was observed when the slides were immersed in air saturated deionized water at room temperature.

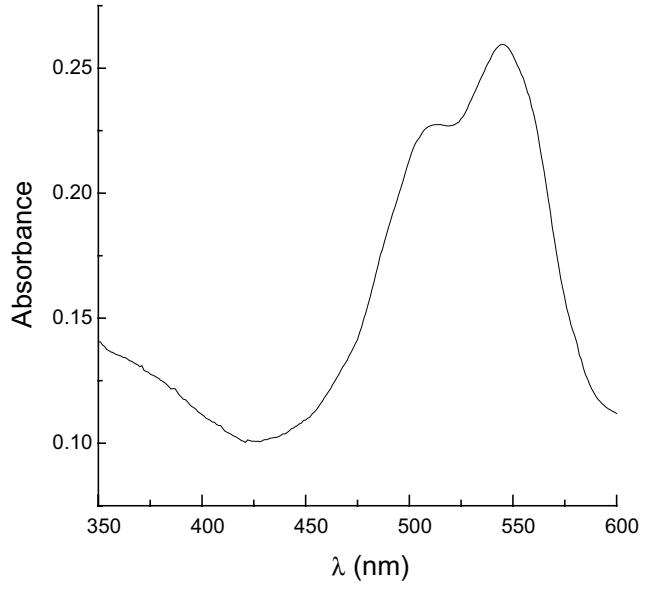

Fig. 3. Absorption spectrum of a dip-coated film of erythrosin B in a fluoropolymer matrix on glass in air.

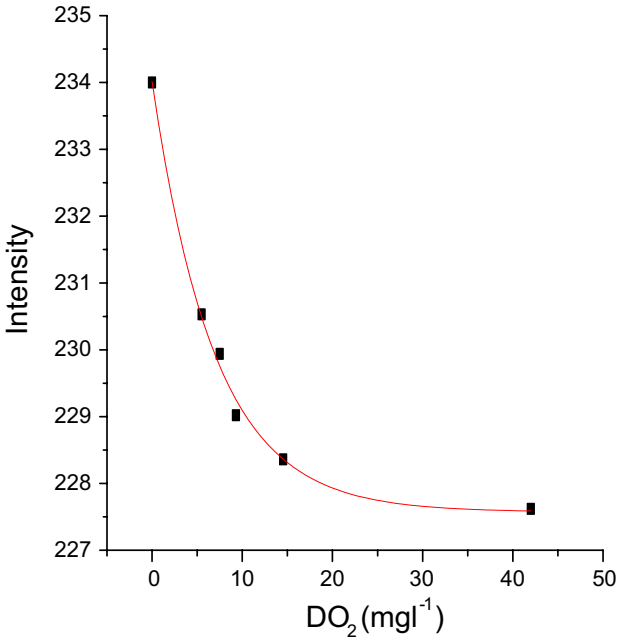

Fig. 4. Variation of phosphorescence intensity (A.U.) of erythrosin B in fluoropolymer matrix at 680 nm with dissolved oxygen concentration.

3.2. Dissolved oxygen sensing

The strong phosphorescence from erythrosin B in the fluoropolymer decreased as the dissolved oxygen concentration increased as shown for example in Fig. 4. The steady-state plots for spin-coated and dip-coated slides all approximately follow first-order kinetics (i.e. are fairly linear) up to about 10 mg l^{-1} of dissolved oxygen. At higher dissolved oxygen concentrations, the plots all exhibit a very marked downward curvature. Stern–Volmer ratios I_0/I from about 0.03 to 0.12 were obtained from the linear parts of the plots for different coated slides corresponding to the ratio of fluorescence emission in deoxygenated to that in oxygen saturated water at 20 °C. The sensor quenching response of a typical sensor, over a range of dissolved oxygen concentrations, is shown as a Stern–Volmer plot in Fig. 5.

From Fig. 4, it can be seen that there is strong residual phosphorescence that is not quenched by the highest concentrations of dissolved oxygen. This may be due to several factors. Some dye molecules may reside in sites in the matrix, which are inaccessible to the quencher. There may be insufficient quencher available to deactivate all the dye molecules or the dye may form aggregates, which are less sensitive or insensitive to dissolved oxygen quenching. Aggregation of dye molecules has been shown to occur previously in polymer matrices which have low glass transitions in which dye diffusion is possible at room temperature. The polymer used for the present work, has a glass transition below room temperature so that aggregation of the dye molecules is possible during the film deposition step. The very broad absorption and phosphorescence

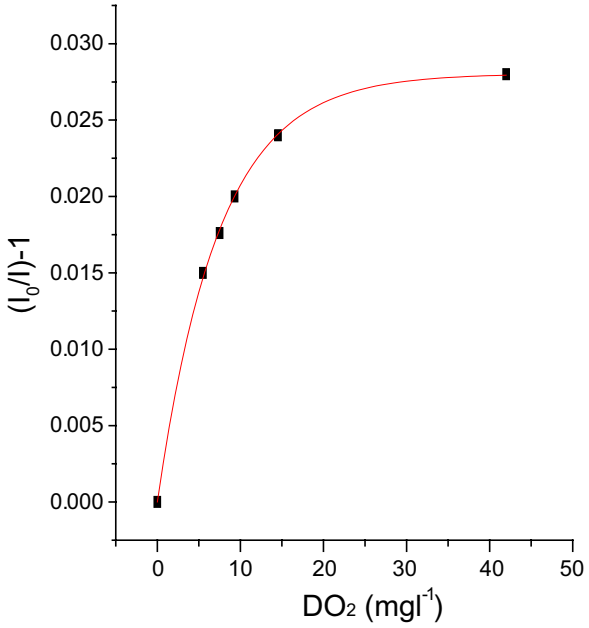

Fig. 5. Stern–Volmer plot for erythrosin B in fluoropolymer matrix. Data fitted by Box–Lucas model with $a = 0.118$ and $b = 0.888$.

spectra of the encapsulated dye are also indicative of a wide distribution of local molecular environments for the erythrosin B.

Usually, curvature in the Stern–Volmer plots at higher oxygen concentrations has been explained by two different theories [19]. The first is the presence of two quenching processes dynamic and static. The second theory assumes dynamic quenching only, but the probe molecules are considered to reside in different sites in the matrix with differing accessibility to oxygen molecules. The presence of aggregates of dye molecules of different sizes with varying sensitivity to the quencher would give rise to similar results.

In the first mechanism, the probe dye is quenched both by excited state collisions, and by ground state complex formation with the quencher. The relative intensity ratio I_0/I is thus given by the product of both dynamic and static quenching.

Thus we have:

$$\frac{I_0}{I} = (1 + K_D[Q])(1 + K_S[Q]) = 1 + K_1[Q] + K_2[Q]^2 \tag{3}$$

where K_D and K_S are the dynamic and static quenching constants respectively and $K_1 = K_D + K_S$ and $K_2 = K_D K_S$.

Thus, this mechanism leads to a quadratic dependence of I_0/I on $[Q]$. Since K_2 is positive however, this leads to an upward curvature in the Stern–Volmer plot. The latter mechanism results in a downward turning Stern–Volmer plot, and is thus more likely to dominate in the present case. Assuming a distribution of dye molecules with varying sensitivity to dissolved oxygen quencher, the SV Eq. (1) can be written

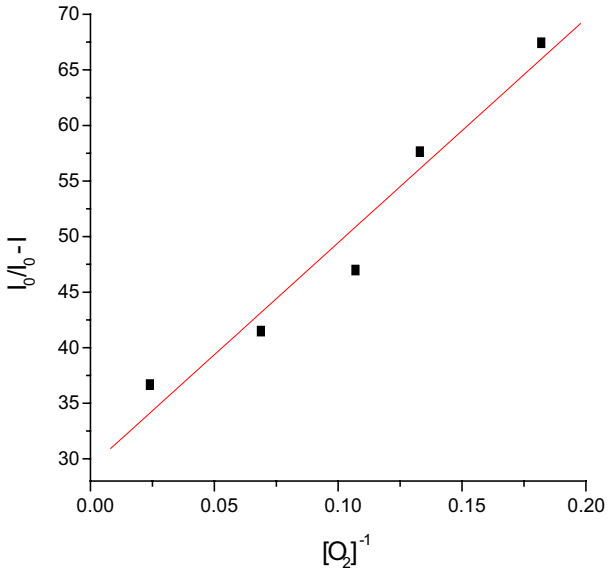

Fig. 6. Modified multi-site Stern–Volmer plot for erythrosin B in a fluoropolymer matrix.

in the form:

$$\frac{I_0}{I} = \left\{ \sum \frac{f_i K_{SVi}[O_2]}{1 + K_{SVi}[O_2]} \right\}^{-1} \tag{4}$$

where f_i is the fraction of dye molecules i, having a quenching constant K_{SVi}.

This may be written as:

$$\frac{I_0}{I_0 - I} = \frac{1}{fK_{SV}[O_2]} + \frac{1}{f} \tag{5}$$

where $f = \Sigma f_i$ which is the maximum mole fraction of dye molecules which are quenched by oxygen. If all erythrosin molecules are quenched to the same degree, $f = 1$.

Using this modified SV equation, plots of $I_0/(I_0 - I)$ against $1/[O_2]$ were constructed.

Fig. 6 shows the data from Fig. 4 plotted in this way. Fairly linear plots were obtained with, in the present example, an intercept $1/f = 25$ and $f = 0.04$. The small fraction of luminescent dye molecules quenched by oxygen, corresponds to the high residual phosphorescence intensity observed in oxygen saturated water.

The Stern–Volmer plots were also accurately fitted by Eq. (6) (Box–Lucas model):

$$\frac{I_0}{I} - 1 = a(1 - b^{[Q]}) \tag{6}$$

where a and b are constants and $[Q]$ is the concentration of dissolved oxygen quencher [20]. This allowed accurate single or double point calibration of the sensor to be readily achieved.

3.3. Probe characteristics

Extended reproducible measurements over several weeks showed that photobleaching was not a significant problem

with this sensor system on this time scale. The slides were however, stored in the dark in closed containers between experiments. No long-term photostability measurements were carried out. The sensors were optically transparent, mechanically stable, though rather soft and rubbery. They were not affected by prolonged immersion in water at room temperature and dye leaching was insignificant.

4. Conclusions

A thin film sensor based on erythrosin B encapsulated in a fluorinated polymer matrix exhibited strong, broad, phosphorescence at 680 nm which was partially quenched by dissolved oxygen in aqueous systems. Residual phosphorescence, which was not quenched by dissolved oxygen, was due to aggregated dye molecules and/or to a distribution of local matrix sites for the dye molecules. The sensor was linear in dissolved oxygen concentration when a multi-site model was used. Dye leaching, photobleaching and light scattering were not significant over the time scales measured. This system shows promise as a relatively inexpensive, easily constructed sensor for the optical detection of dissolved oxygen in aggressive aqueous environments. Although there was strong background phosphorescence, it did not compromise the sensitivity of the detector since good signal-to-noise (S/N) ratios ($\geq$50) in the Stern–Volmer plots were still obtained with excitation and detector slit widths of 10 nm. The S/N ratios achieved, will however depend on the optical configuration employed in the final instrument. The background signal was however stable and could be subtracted if necessary. The detector will be most useful at the low dissolved oxygen concentrations ($\leq 9\,\mathrm{mg\,l^{-1}}$) found in aqueous systems were the Stern–Volmer plot is almost linear. The long phosphorescent lifetimes of the indicator dye also facilitate the use of phase-shift lifetime measurements as alternatives to the steady-state intensity techniques used.

Presently, work is underway using fluoropolymer/sol–gel composites as hosts for the dyes. These seem to improve the physical properties and quenching characteristics without compromising the desirable protectant properties of the matrix.

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