Effect of Lumophore and Plasticiser Concentration on The Heterogeneity of Oxygen Quenching in Thin Film Oxygen Sensors

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Kinetic heterogeneity of the luminescence decay and oxygen quenching of Pt and Pd octaethylporphyrin/ethyl cellulose (OEP/EC) thin film oxygen sensors has been investigated with respect to (a) concentration of lumophore and (b) addition of plasticiser. The source of kinetic heterogeneity shown by PtOEP films under N_2 is a monomer–dimer equilibrium in which the dimer luminescence decays with $k = 0.0527 \times 10^6$ s^{-1} and the monomer luminescence with $k = 0.0101 \times 10^6$ s^{-1} and $K_D = 790$ (± 20) mol dm^{-3}. For PdOEP/EC films there is no detectable aggregation and luminescence decays under N_2 show good fits to single exponential curve fits at all concentrations studied. The addition of either tripbutyl phosphate or dimethylphthalate as plasticiser does not decrease kinetic heterogeneity for oxygen quenching of luminescence in the films.

INTRODUCTION

There has been much interest in the use of polymer encapsulated oxygen-quenched lumophores as optical oxygen sensors in which there is an $[O_2]$ dependent reduction in luminescence intensity as a consequence of oxygen quenching of the emitting state [1–4]. In general the results of such studies are discussed in terms of Stern–Volmer analysis of emission data.

For a homogeneous system with lumophore, L, which decays naturally by a first order process, k_{uq}, and which is dynamically quenched by oxygen, with a rate constant k_q, the rate of decay of the excited state of the lumophore, L^*, is given by:

$$- \mathrm{d}[L^*]/\mathrm{d}t = (k_{uq} + k_q[O_2])[L^*] \qquad (1)$$

For a homogeneous system, the decay of luminescence is expected to decay exponentially and there should be a linear relationship between the quenching efficiency, i.e. I_0/I or τ_0/τ, and $[pO_2]$. Given by

$$I_0/I = 1 + \tau_0 k_q[O_2] \qquad (2)$$

Where I_0 is the emission intensity in the absence of oxygen, I is the emission intensity in the presence of oxygen, τ_0 is the lifetime in the absence of oxygen and k_q is the bimolecular rate constant for oxygen quenching. The equivalent kinetic equation sees I_0/I replaced with τ_0/τ, where τ is the lifetime in the presence of oxygen at concentration $[O_2]$.

However, two common features of oxygen quenching for almost all polymer/lumophore combinations are: a non-exponential emission decay in the presence of oxygen and a non-linear relationship between I_0/I or τ_0/τ and pO$_2$, the partial pressure of oxygen [5,6–9]. Such behaviour is usually discussed in terms of heterogeneity in which the lumophore is considered to occupy a distribution of sites. These sites differ in one or

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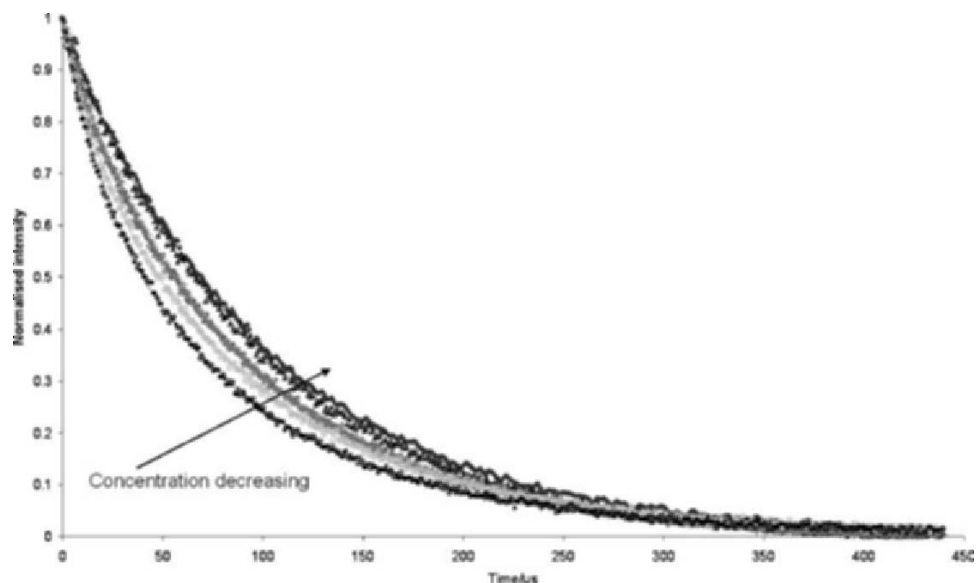[2] To whom correspondence should be addressed. E-mail: 175249@ swan.ac.uk

Fig. 1. Time resolved emission decay curve of PtOEP in PtOEP/EC films in the absence of oxygen. Open symbols—experimental decay curves; solid lines—curve fit analysed by Tablecurve^{TM}2d. Concentrations of PtOEP in the film: 1.24–49.6×10^{-5} mol dm^{-3}.

more property such as diffusion of oxygen (D_{O_2}), solubility of oxygen (S_{O_2}), τ_0 and k_q within the film. Modelling the luminescence decay kinetics has been the subject of much work. Approaches include a dual site model, continuous distribution models such as Gaussian or log Gaussian, and semi-empirical equations adapted from adsorption studies of heterogeneous systems such as the Freudlich isotherm. [3–5] Understanding this kinetic heterogeneity is an important step in understanding the response characteristics of these sensors. [4]
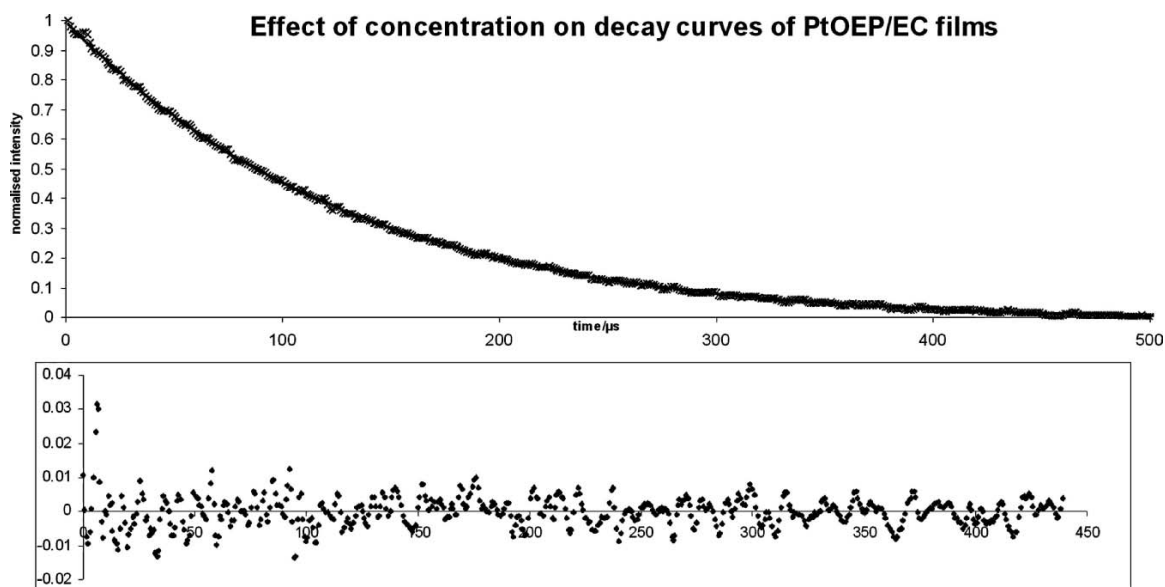

Fig. 2. Emission decay curve for low concentration (1.24×10^{-5} mol dm^{-3}) PtOEP in PtOEP/EC film under N$_2$, with single exponential decay curve as solid line, with corresponding residuals as analysed Tablecurve^{TM}2d. At this concentration, there is very little aggregation and this curve gives $k = 0.0101 \times 10^6$ s^{-1} for monomer PtOEP.

In studies aimed at optimising sensor response much use has been made of plasticisers [10] and while plasticisers are known to generally increase film sensitivity, little is known of their effect on heterogeneity within the film.

We previously reported results from studies of oxygen quenching of palladium and platinum octaethylporphyrin (PdOEP, $\tau_0 \sim 1400$ μs; PtOEP, $\tau_0 \sim 100$ μs) luminescence in unplasticised ethyl cellulose (EC) films. [5,10] We found that:

1. in the absence of oxygen the decay curves of PtOEP are not perfect fits to a single exponential except at very low PtOEP concentrations, while those for PdOEP are much better fits;

2. for both PdOEP and PtOEP the decay curves in the presence of air are very poor fits to a single exponential.

In this work, we present results from time resolved studies on the effect of lumophore concentration (1.24–49.6 × 10^{-5} mol dm^{-3}) and polymer/plasticiser formulation on film heterogeneity for PtOEP and PdOEP in EC films. We show that: the kinetic heterogeneity for PtOEP in EC in the absence of oxygen arises from aggregation, that in the absence of oxygen PdOEP does not aggregate and shows good mono-exponential decays over the same concentration range, and that the plasticisers examined do

not reduce the kinetic heterogeneity observed for these films in the presence of oxygen.

METHODS AND MATERIALS

Ethylcellulose (EC) (46% ethoxy content); and PdOEP were obtained from Aldrich. PtOEP was obtained from Porphyrin Products Ltd. (Logan, UT, USA). Tributyl phosphate (TBP) and dimethyl phthalate (DMP) were supplied by Acros chemicals.

O_2 and N_2 were BOC 'high purity' gases, and were used, as received.

Gas mixtures from 0–100% air were generated using a gas blender (model no. 852 V1-B, Signal Instruments Co, UK) with nitrogen as the diluent gas. Purging was carried out before each measurement to allow equilibration between the gas stream and the film.

Oxygen sensors were prepared by spin coating onto glass slides an ethyl cellulose (EC) solution containing varying concentrations of platinum octaethylporphyrin (PtOEP) or palladium octaethylporphyrin (PdOEP) and, when required, a plasticiser, i.e. either tributyl phosphate (TBP) or dimethyl phthalate (DMP). [5,10] Plasticiser concentrations are given in parts per hundred resin (i.e. EC) (pphr).

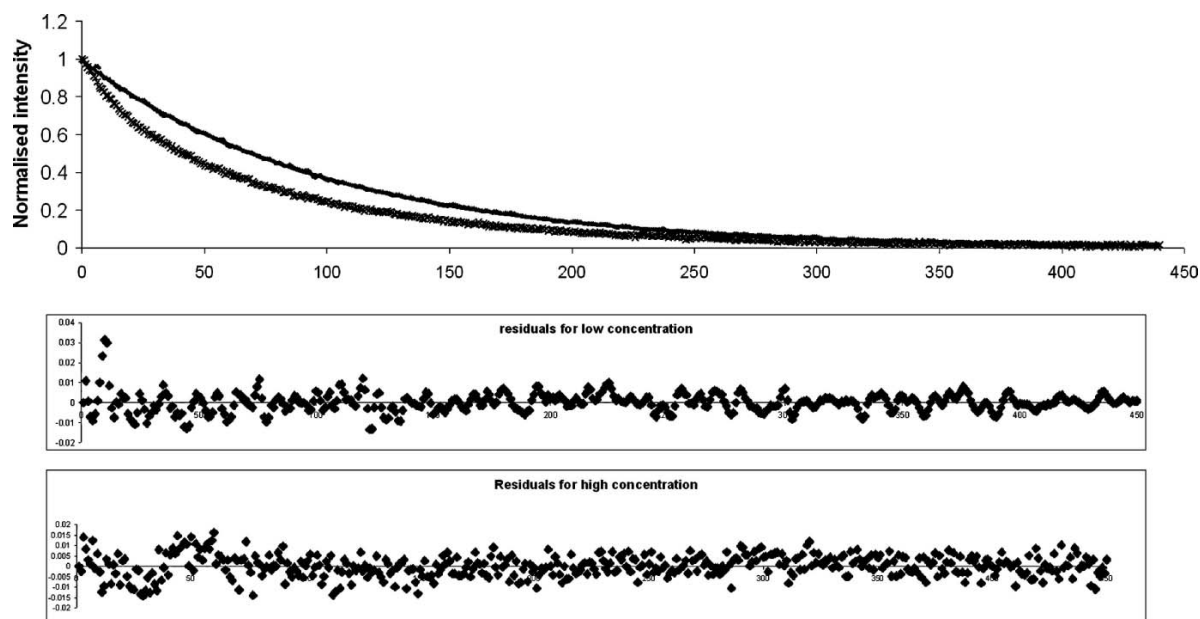The 532 nm line of a Q-switched Nd/YAG laser was used for excitation,. Emission wavelengths of 644 and

Fig. 3. A Emission decay curves for lowest and highest concentration of PtOEP in PtOEP/EC films under N_2. Curve fit to double exponential fit of the form $Y = A + \alpha_1 e_1^{-kt} + \alpha_2 e^{-kt}$, where k_1 and k_2 equal 0.0527×10^6 s^{-1} and 0.0101×10^6 s^{-1} respectively, shown as solid lines. B and C give residuals.

Table I. Amplitudes of the fixed rate constants from a double exponential analysis $[(Y = A + \alpha_1 e^{-k_1 t} + \alpha_2 e^{-kt})$ where k_1 and k_2 are fixed at 0.0527 and 0.0101×10^{-6} s$^{-1}]$ of time resolved emission from PtOEP/EC film at 0 torr.

	Percentage contribution	
(Porphyrin)(10^{-5} mol dm^{-3})	$\alpha_1 \, k_1 = 0.0527 \times 10^{-6}$ s^{-1}	$\alpha_2 K_2 = 0.0101 \times 10^{-6}$ s^{-1}
1.24	1.1	98.9
3.10	2.2	97.8
6.20	11.2	88.8
12.4	13.8	86.2
24.8	23.8	76.2
49.6	33.9	66.1

665 nm were used for PtOEP and PdOEP respectively. All work was carried out using slit widths of 36 nm with averaging of 32 decay curves.

Curve fitting was carried out using Tablecurve^{TM}2d by Jandel Scientific.

RESULTS AND DISCUSSION

Time Resolved Emission Data

The time resolved emission decay curves for the PtOEP/EC films of increasing concentration obtained un-

der N$_2$ are shown in Fig. 1. The lifetime decreases with concentration as does the goodness of fit to a single exponential decay.

Figure 2 shows the results of the decay curve of the lowest PtOEPconcentration (1.1×10^{-5} mol dm^{-3}) fitted with a single exponential decay. The best fit gives $k = 0.0101 \times 10^6$ s^{-1}. At higher concentration a single exponential fit is inadequate, but free fitting shows that all decay curves can be well fitted a double exponential with one component of $k \, ca.$ 0.010 (± 0.002) $\times$ 10^6 s^{-1} and the other with $k \, ca.$ 0.050(± 0.001) $\times 10^6$ s^{-1}. This constancy of rate constants suggests the presence
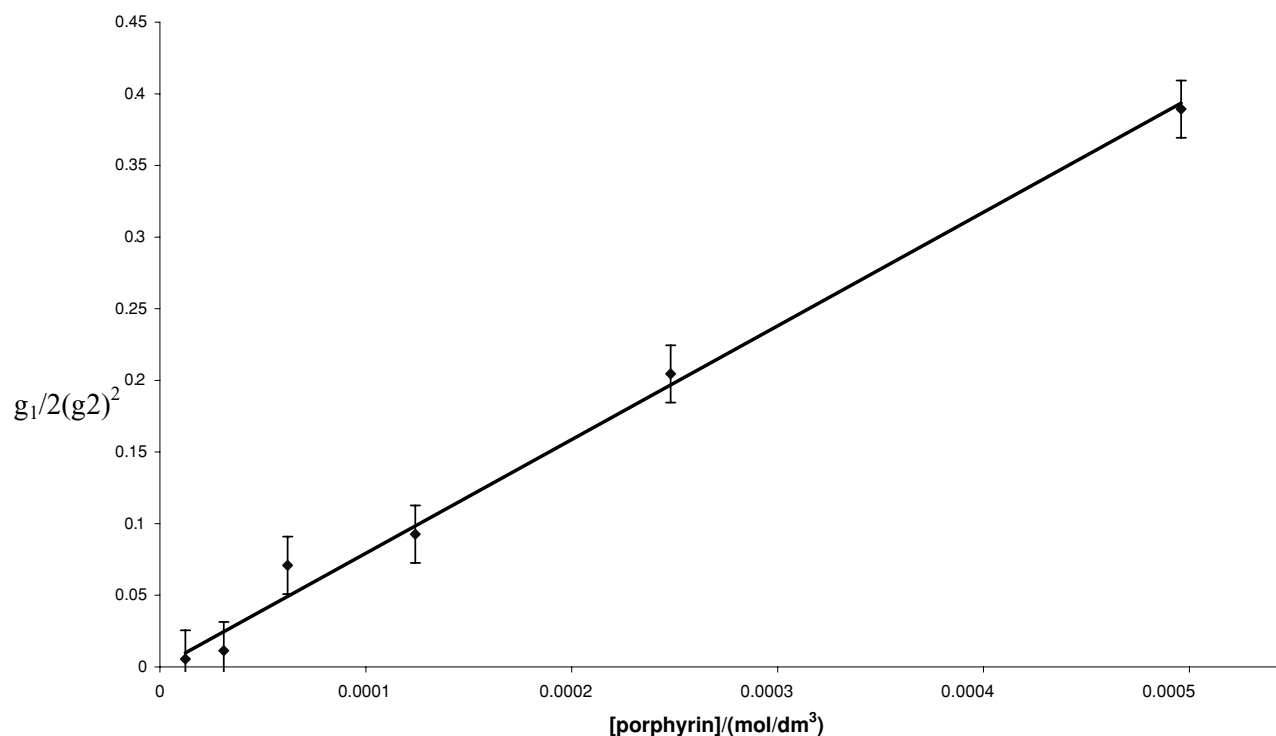

Fig. 4. Plot of $\alpha_1/2(\alpha_2)^2$ vs [PtOEP] in PtOEP/EC film. The gradient is equal to K_D. The data give $K_D = 790 \pm (20)$ mol^{-1} dm^3.

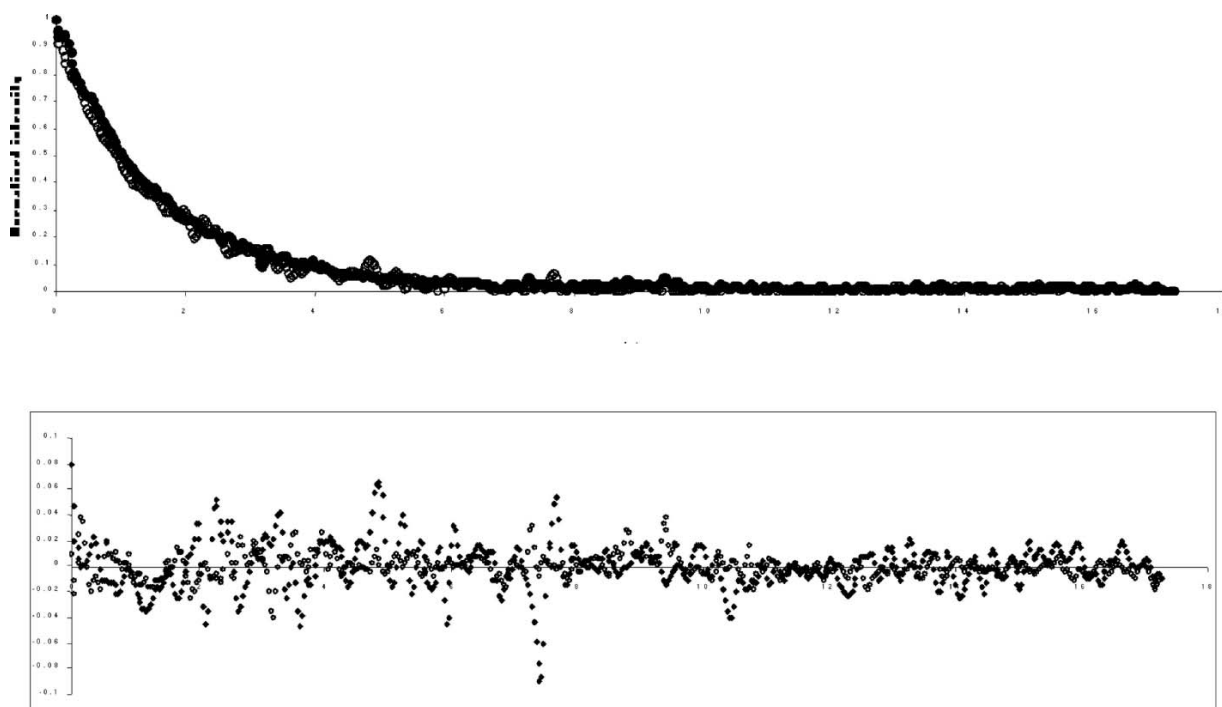**Fig. 5.** Emission decay curves and residuals for lowest (open circles, PdOEP $= 1.2 \times 10^{-5}$ mol dm^{-3}) and highest (closed circles, PdOEP $= 5 \times 10^{-4}$ mol dm^{-3}) concentration of PdOEP studied in PdOEP/EC films under N$_2$. Solid lines are fits to single exponentials.
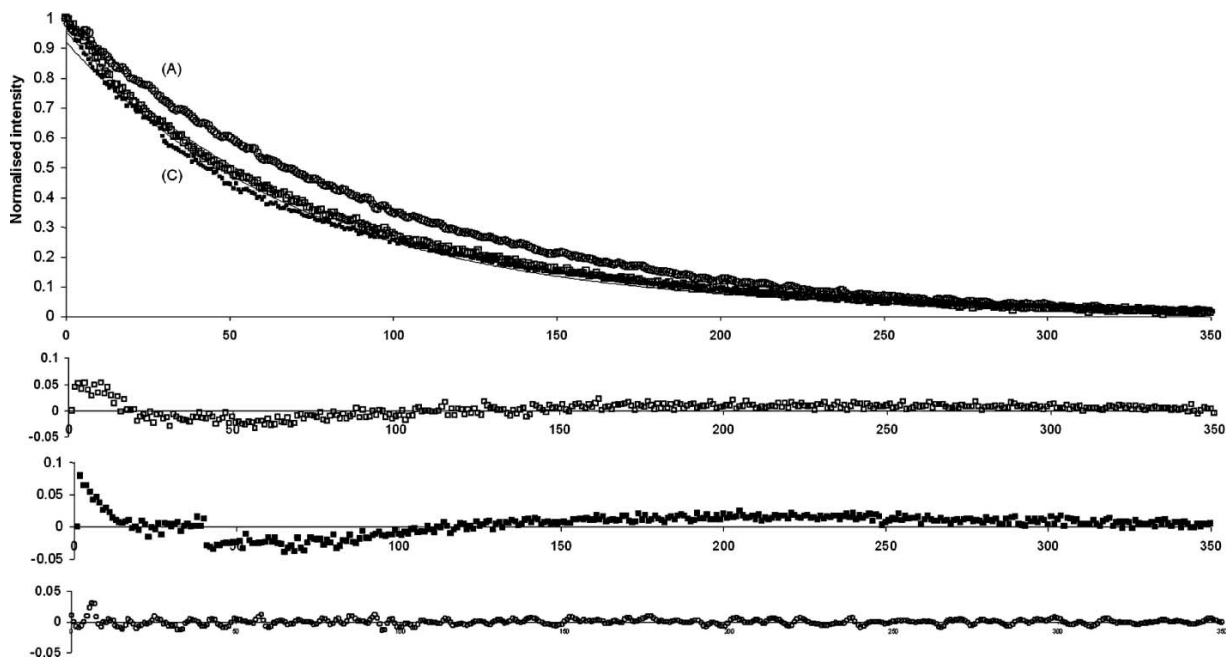

Fig. 6. Emission decay curves and residuals for PtOEP in PtOEP/EC/plasticiser films under N$_2$. ($\bigcirc$ = unplasticised films, $\square$ = 50 pphr TBP and $\blacksquare$ = 50 pphr DMP).
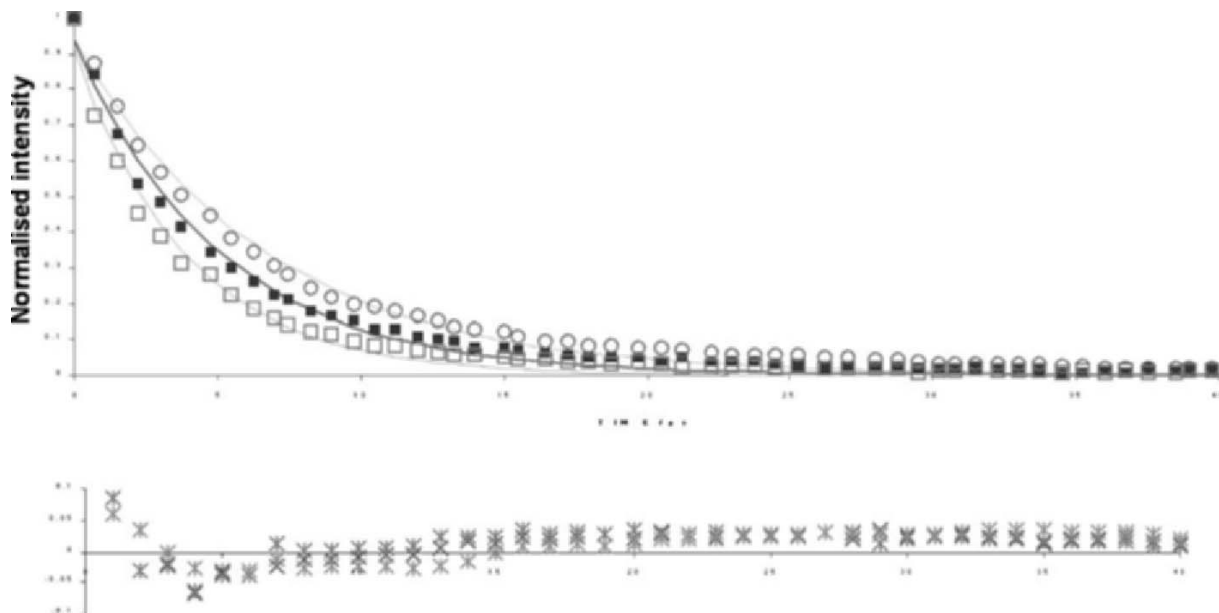
Fig. 7. Emission decay curves and residuals for PtOEP in PtOEP/EC/plasticiser films under O_2. ($\bigcirc$ = unplasticised films, $\square$ = 50 pphr TBP and $\blacksquare$ = 50 pphr DMP).

of just two species; a monomer and aggregate, perhaps a dimer.

In order to examine this possibility, a global analysis using fixed rate constants and variable amplitudes was applied to the data, and the amplitudes analysed as follows. If there is an equilibrium of the form $2M = D$, then a plot of $\alpha_1/2(\alpha_2)^2$ against PtOEP concentration, where α_1 corresponds to the dimer component and α_2 corresponds to the monomer, will be linear with slope = K_D. Rate constants of $k_1 = 0.0527 \times 10^6$ s^{-1}, $k_2 = 0.0101 \times 10^6$ s^{-1} were chosen from the averages of those obtained from the free fitting shown in Fig. 3, and using these the percentage contribution of each component was obtained as given in Table I. A plot of $\alpha_1/2(\alpha_2)^2$ against [PtOEP] is shown in Fig. 4, it shows good linearity from which a value of 790 ($\pm$20) mol^{-1} dm^3 is obtained for K_D.

In contrast to PtOEP films, PdOEP in EC films under N_2 gives identical exponential decay curves across the concentration range studied (Fig. 5).

It is worth noting here that the decay curves from either PtOEP or PdOEP in EC in air at any concentration studied here give very poor fits to both single and double exponentials as observed previously. This has previously been assigned to heterogeneity in k_q within the films, [9], and thus dimerisation of PtOEP seems to have little effect on the heterogeneity arising from this source.

EFFECT OF PLASTICISERS

Plasticisers have been widely used in thin polymer film sensors to influence sensor response [11]. Plasticiser–polymer compatibility is determined by the relative strengths of the intermolecular forces between and within the plasticiser and polymer. Some measure of this is given by the difference in solubility parameter, δ, of plasticiser and polymer [11,12]. For this study we chose two plasticisers of different δ values:. δEC, δDMP, and δTBP = 21.1, 22.2, and 17.5 (J cm^{-3})$^{1/2}$, respectively.

Figure 6 shows PtOEP decay kinetics in plasticised polymer films under nitrogen. They are worse fits to exponential than comparable concentrations in the absence of plasticiser, suggesting an increase in kinetic heterogeneity. By way of contrast, plasticised PdOEP films give good first order decays under nitrogen, although the lifetime is reduced in plasticised films (e.g. to 1310 (s in the 50 pphr TBP plasticised film).

EFFECT OF PLASTICISER ON DECAY KINETICS UNDER O_2

Figure 7 shows the decay kinetics for PtOEP in plasticised polymer films under oxygen. Although the emission decay is faster in the plasticised films, there is no obvious decrease in heterogeneity.

CONCLUSIONS

The kinetic heterogeneity observed for PtOEP/EC sensor films under nitrogen has been shown to be due to a monomer:dimer equilibrium for which the kinetic data can be analysed in terms of two exponentials with $k_1 = 0.0527 \times 10^6$ s^{-1} (dimer), $k_2 = 0.0101 \times 10^6$ s^{-1} (monomer) and $K_D = 790 \ (\pm 20)$ mol^{-1} dm^3. In contrast, for PdOEP in PdOEP/EC films there is no detectable aggregation with good fits to single exponential curves at all concentrations studied.

The addition of either tripbutyl phosphate or dimethylphthalate as plasticisers does not decrease kinetic heterogeneity for oxygen quenching of luminescence in the films.

ACKNOWLEDGMENT

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