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Luminescence quenching of Ru(II) complexes in polydimethylsiloxane sensors for oxygen

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Abstract

The luminescence quenching of ruthenium(II)-tris(1,10-phenanthroline) and ruthenium(II)-tris(4,7-diphenyl-1,10-phenanthroline) by oxygen in films of commercial polydimethylsiloxane was studied by steady state and time-resolved methods. The decay kinetics is not monoexponential in the absence and in the presence of oxygen. It can be accurately described in all cases by the function $\exp(-Bt^{1/2})$, a particular case of the stretched exponential behaviour often found in solid media. The steady state and integrated time-resolved quenching efficiency coincide and show a downward curvature as a function of oxygen partial pressure. This dependence is explained by assuming a Freundlich type adsorption of oxygen in the dopants of the polymer. Both complexes render the same dependence of adsorbed oxygen on its partial pressure. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Luminescence; Quenching; Oxygen; Ruthenium(II) diimines; Polymer

1. Introduction

The determination of oxygen levels in gaseous, aqueous and biological samples is of great importance in environmental, industrial and biomedical fields. In the past, most oxygen measurements were based on the Clark electrode [1], although the Winkler titration was also widely used [2]. The Winkler titration is slow and cumbersome, and interferences are numerous.

Since the past decade, luminescence of transition metal complexes has formed the basis of a class of oxygen sensors using oxygen deactivation of the emission. The major advantages of luminescence based oxygen sensors over the Clark electrode are small size, lack of oxygen consumption and reference cells, and avoiding electrode poisoning by proteins and various organic compounds.

The use of luminescent transition-metal complexes as spectroscopic probes and sensor materials has received considerable attention in recent years [3]. Particularly, there is a growing interest in optical sensors for the detection of oxygen [4–11].

The choice of the dye whose luminescence is quenched by oxygen has been dominated by the Ru(II) diimine complexes: ruthenium(II)-tris(4,7-diphenyl-1,10-phenanthroline) ($Ru(dpp)_3$) and ruthenium(II)-tris(1,10-phenanthroline) ($Ru(phen)_3$), which have proved to be the most successful to date [12–19]. These materials have very desirable features. They are photostable and produce electronically excited states with long lifetimes ($\tau_0 = 5$ μs and 1 μs for $Ru(dpp)_3$ and $Ru(phen)_3$, respectively). These complexes show intense visible absorption, which involve metal-to-ligand charge transfer (MLCT) transitions. All major emission contributions in these systems arise from the lowest triplet state, which is efficiently deactivated by oxygen.

Since these excited states are also highly sensitive to environment, the luminescence quantum yield and lifetime will also respond to metal ions, oxidants, reductants, proteins, etc. Oxygen sensors systems must separate the dye from all interference while still allowing oxygen access.

The simplest method is to put the dye into a gas-permeable, solvent-impermeable membrane. Usually, the oxygen-sensitive dyes are dissolved in a polymer matrix which immobilizes them. Desirable matrix properties include high permeability to oxygen, mechanical and chemical stability, and high solubility of the indicator. Silicone rubber is especially useful because of its permeability to oxygen, many times greater than any other organic polymer [4] and high chemical and mechanical stability. This polymer, with a hydrophobic nature, also provides means to improve

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sensor selectivity in being impermeable to ionic species and additionally it reduces dye leaching.

These oxygen sensors use luminescence spectroscopy for sensing, by quenching of either steady-state intensity or lifetime. In polymer matrices the decay kinetics of the luminescence deviates, even in the simplest case, from a single exponential [20,21]. Nonlinear Stern–Volmer quenching plots are characteristic of solid state supports, as opposed to solution where the usual linear behaviour is observed.

The problem of mechanistically interpreting the decay kinetics is complex in the solid phase [20–23]. Approaches using a multiple sum of exponential terms gave acceptable fits but yielded no physical basis for understanding the kinetics. Even if the multiexponential fit is replaced by a Gaussian distribution of lifetimes, no reasonable dependence of the parameters on oxygen concentration was obtained [16].

A model was developed to describe the fluorescence decay of indicator molecules based on the influence of the microenvironment [19]. The authors propose the following function to describe the time dependent luminescence of Ru(dpp)$_3$ in polymers:

$$I(t) = I_o \exp(-kt - C\sqrt{t}) \qquad (1)$$

where C and k are adjustable parameters. The origin of C is in matrix-dye interactions by an energy-transfer mechanism by off-resonance electromagnetic coupling. The term in k includes a dynamic quenching parameter, proportional to the oxygen concentration.

In this work, steady state and time resolved luminescence measurements of Ru(dpp)$_3$ and Ru(phen)$_3$ in commercial polydimethylsiloxane (PDMS) were performed. We propose a kinetic algorithm with only one decay term, which gives excellent fits of the luminescence decay curves for both complexes, using one oxygen-dependent parameter. The correlation of this parameter with the oxygen partial pressure (P_{O_2}) is the same for both dyes and it shows a saturation behavior. This dependence can be explained by assuming a Freundlich type adsorption of oxygen.

2. Experimental section

2.1. Materials

The following reagents were used as obtained from the reported sources: Ruthenium(II)-tris(1,10-phenanthroline)-dichloride: Aldrich; sodium dodecylsulfate (DS): Sigma; Ruthenium(II)-tris(4,7-diphenyl-1,10-phenanthroline)-dichloride: G. Frederick Smith Chemical; polyester foil (Mylar): Dupont; chloroform: Nedma (analytical grade); silicone prepolymer (transparent, acetic acid releasing Silicone E-4): Wacker.

Ruthenium(II)-tris(1,10-phenanthroline)(DS)$_2$ was precipitated from an aqueous solution of Ruthenium(II)-tris(1,10-phenanthroline)Cl$_2$ by DS addition, as described by [17].

The gases used, nitrogen and oxygen, were of high purity and were purchased from AGA (Argentina). Gas mixtures of O$_2$ and N$_2$ of the desired concentration were prepared by flux mixing of the two gases in a chamber placed immediately before the sample compartment containing the sensor. The amount of each gas was regulated by a valve and measured by two calibrated flow meters of nitrogen and oxygen before entering the mixing chamber. Total pressure was always 1 atm, and P_{O_2} was varied between 0.00 and 1.00 atm.

2.2. Preparation of sensing films

The oxygen sensing films were made by preparing Ru-complex and silicone mixtures of about 1% w/w of dye, and dissolving the mixture in a volume of chloroform enough to reach an adequate viscosity. The final, solvent-free film was prepared by spin coating the viscous solution onto a Mylar support and drying at 40°C for 24 h. Homogeneous layers of a few μm were obtained.

2.3. Instrumentation

Steady-state luminescence intensity measurements were performed using a PTI Quantamaster luminescence spectrometer. For steady state intensity measurements, the wavelengths of excitation and emission were 450 and 600 nm, respectively.

Time resolved luminescence measurements were made using a Nd:YAG (Spectron Laser, 8 ns FWHM). An excitation wavelength of 532 nm was used. A neutral density wedge attenuated the laser beam energy to a suitable value. Emission was filtered by a 570 nm cut-off filter (Schott OG570) before being focused by a *f*/0.6 aspherical lens into a fiber optic. Wavelength was selected by a monochromator and light was measured with a photomultiplier tube (Hammamatsu R928). Most kinetic decays were monitored at 600 nm. The emission trace was collected and averaged on a Hewlett Packard 54502A digitizing oscilloscope and transferred to a computer for kinetic analysis.

The sensing films were mounted into a luminescence cell equipped with a stopper which had inlet and outlet needles to allow gas flow. The geometry of decay time measurements involved a ca. 30° angle of incidence for the excitation laser pulse relative to the plane of the sensing film and a 90° angle between excitation pulse and emission detection.

All measurements were performed at room temperature, without temperature regulation.

2.4. Results and discussion

Fig. 1 shows luminescence decay curves of Ru(phen)$_3$ and Ru(dpp)$_3$ in the presence and in the absence of oxygen. The four curves are fitted to a time dependent luminescence signal, $I(t)$, given by Eq. (2)

$$I(t) = I_0 \exp(-B\sqrt{t}) \qquad (2)$$

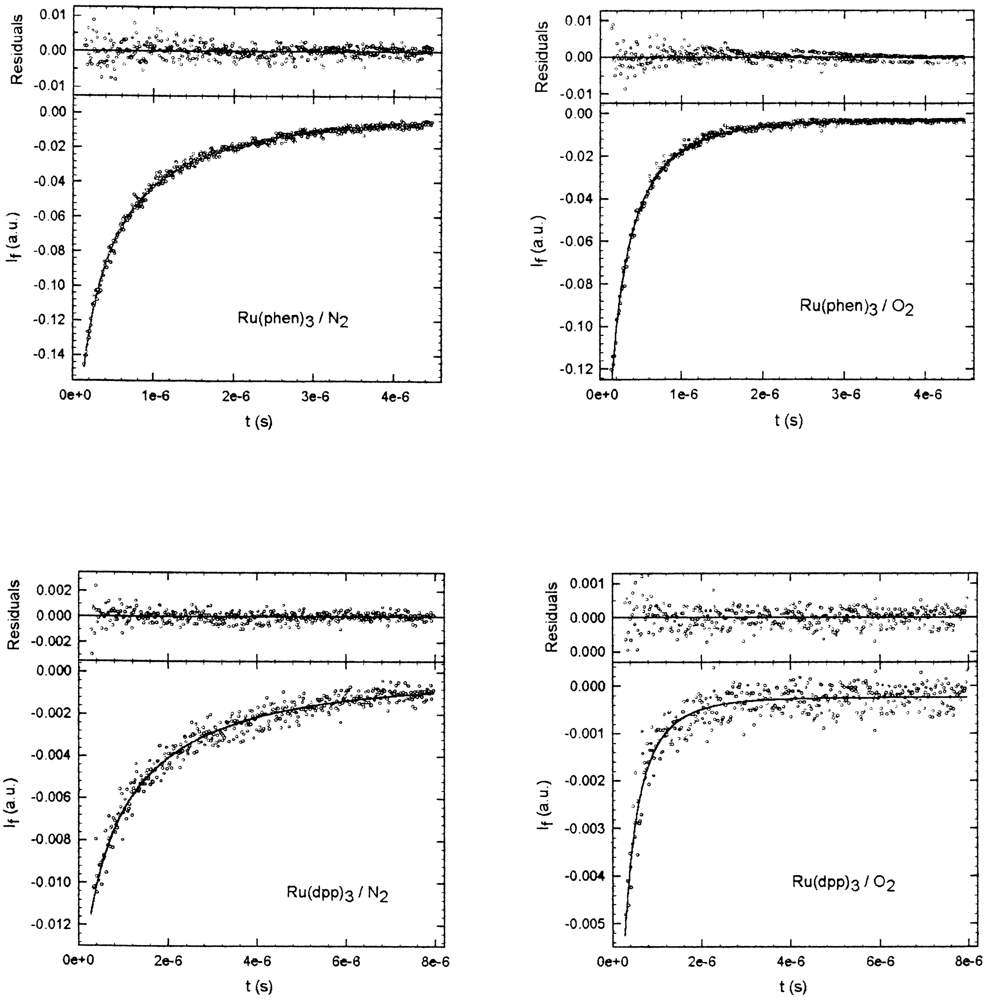

Fig. 1. Luminescence decay of $Ru(phen)_3$ and $Ru(dpp)_3$ in polydimethylsiloxane films in contact with pure gases, as indicated $\lambda_{exc} = 532$ nm, $\lambda_{obs} = 600$ nm.

where the parameter B depends on P_{O_2}. This simple function fits the decay curves very well as measured by χ^2 and distribution of residuals, which are plotted above each curve.

Steady state Stern–Volmer plots are non-linear with a downward curvature, as shown in Fig. 2. The steady state results coincide with the model independent time-integrated decay curves as is also shown in Fig. 2. This excludes the possibility of static quenching. This fact was expected taking into account that the complexes emit from a triplet state which is formed with unitary quantum yield [24].

The luminescence decay of $Ru(dpp)_3$ in silicon rubber films was fitted by Draxler and Lippitsch [19] to a more complex function Eq. (1).

This equation is not needed to describe the present experiments as can be better seen by transforming Eq. (1) to a linear form:

$$-\frac{1}{t}\ln\left[\frac{I(t)}{I_0}\right] = k + C\frac{1}{\sqrt{t}} \qquad (3)$$

The representation of the results of Fig. 1 according to the linear form of Eq. (3) is shown in Fig. 3. For both complexes, the intercept of the representation is negligible, indicating that the decays can be described satisfactorily by Eq. (2).

The dependence of the kinetic parameter B of Eq. (2) on P_{O_2} is represented for both complexes in Fig. 4. They show a saturation effect, which is reached at a different P_{O_2} for both complexes.

The reason of this downward curvature can be either a concentration effect or a kinetic effect. If the concentration of oxygen is not linear with P_{O_2}, then the quenching efficiency can drop as a function of P_{O_2}. The possibility of this effect was mentioned to explain similar results as ours [16].

Downward curvature of Stern–Volmer plots is found when different locations of the excited state are dynamically quenched with different efficiency [25]. This situation is often encountered in solid phase and in microheterogeneous systems. The simplest model, involving normally a small number of different sites, leads to a time-resolved luminescence decay that is a sum of exponentials. Draxler et al [16] demonstrated that a sum of exponential terms leads to cumbersome description of experimental results for the quenching of

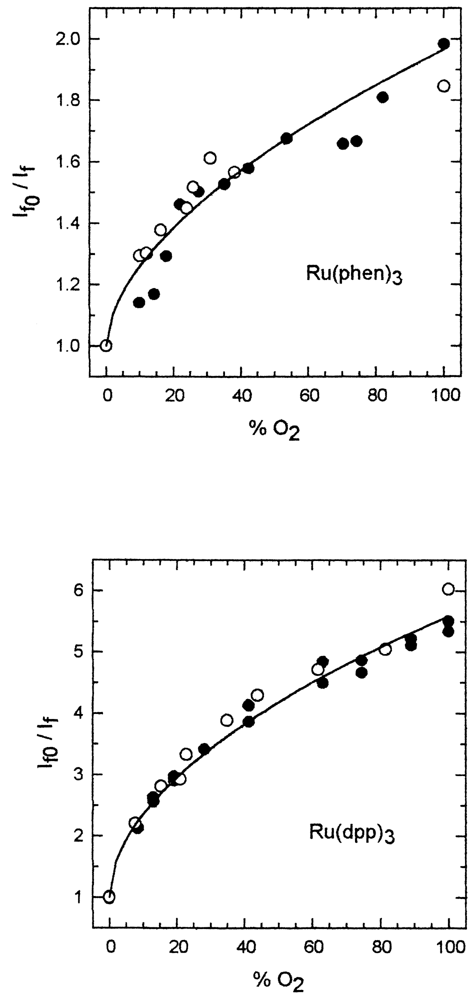

Fig. 2. Stern-Volmer plots of the quenching of Ru(phen)$_3$ and Ru(dpp)$_3$. (○) integrated from the luminescence decay data; (●) steady-state measurements. The lines are the best fits according to Eq. (10). (See parameters in Fig. 5).

Ru(dpp)$_3$ in polymers. This is also valid for our results. The conclusion is that a more complex model is needed.

To analyze the conditions that this model must satisfy we have to take first into account that the decay of the two complexes in the absence of oxygen follows an exponential law with a fractional exponent of the time. This is a particular case of the stretched exponential law frequently found in many processes in polymers [20,26,27].

$$I(t) = I_0 \exp[-(t/\tau)^{\alpha}] \quad (4)$$

The origin of the stretched exponential is the microheterogeneity of the solid phase and the departure of the parameter α from one is a direct measure of the microheterogeneity. In all measured decays, when fitted to Eq. (4), α was very near 0.5. The first consideration to be taken into account then is that the unquenched decay of the probes is not a single exponential due to microheterogeneity of the matrix.

From a kinetic point of view, there are two analytical situations in which $\alpha = 0.5$ can be derived: (1) Förster-type resonance energy transfer [28], and (2) non-steady state diffusion of a quencher [29]. These two models predict a decay law like Eq. (1), including in the exponential the sum of a linear term, accounting for the decay of the unquenched probe, and a $\sqrt{t}$ term, originated in the quenching process.

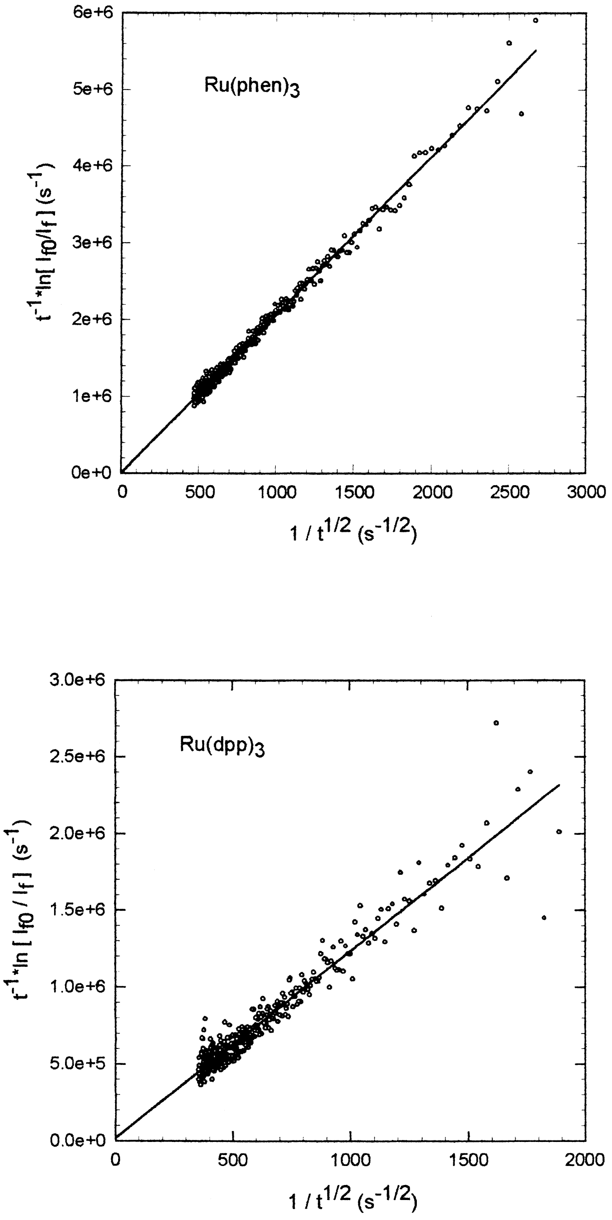

Fig. 3. Representation of the decays obtained in pure nitrogen of Fig. 1 according to Eq. (3) (see text), for Ru(phen)$_3$ and Ru(dpp)$_3$.

The expression for the Förster-type resonance energy transfer quenching is:

$$I(t) = I_0 \exp\left[-\left(\frac{t}{\tau_0}\right) - \sqrt{\pi}\left(\frac{c}{c_0}\right)\left(\frac{t}{\tau_0}\right)^{1/2}\right] \quad (5)$$

where c is the acceptor concentration, c_0 is a critical transfer concentration parameter, and τ_0 is the fluorescence lifetime in the absence of quencher (assuming the decay to be

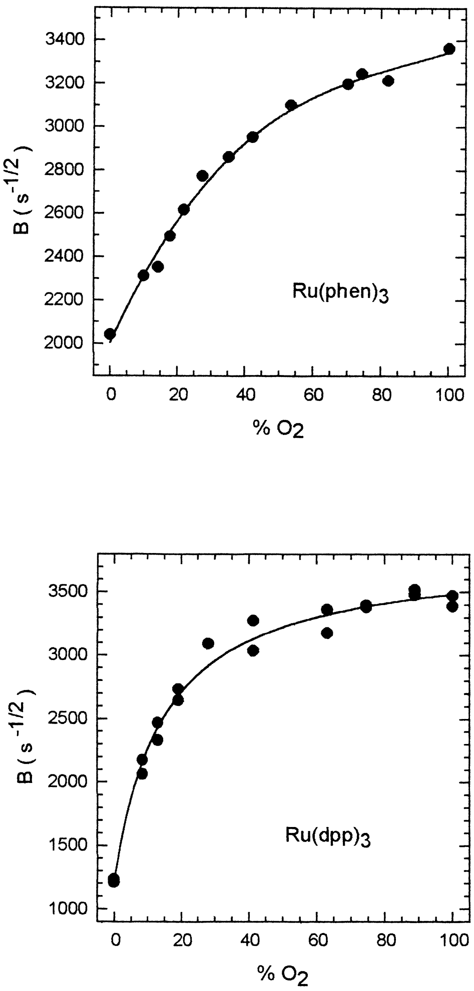

Fig. 4. Quenching parameter B (from Eq. (2)) as a function of oxygen partial pressure for Ru(phen)$_3$ and Ru(dpp)$_3$. Total pressure was always 1.00 atm.

monoexponential). Draxler et al [19] considered that polymer sites act as energy acceptors (c is their concentration in this model), deactivating the excited state in a microheterogeneous way. Eq. (5) is similar to Eq. (1) and explains the decay law observed in the absence of oxygen in their case. Our results in the absence of oxygen could be explained assuming that the second term in the exponent of Eq. (5) is much bigger than the first one during the whole decay for the two complexes. This statement cannot be tested as there is no possible estimation of either c or c_0.

In the presence of oxygen, a term $k_q c' t$ is added to the exponent in Eq. (5) to take into account the dynamic quenching by oxygen (at a concentration c'). They see no change in the $\sqrt{t}$ term with P_{O_2}. On the contrary, as stated above, we do observe a change in the coefficient of $\sqrt{t}$ and the term linear in time must be always negligible in the exponential of Eq. (5) in order for it to coincide with Eq. (2). But we still have to justify the presence of a quenching process proportional to $\sqrt{t}$.

The expression for the non-steady state diffusion quenching is:

$$I(t) = I_0 \exp\left[-\left(\frac{1}{\tau_0} + 4\pi D r_0 c'\right)t - 8\sqrt{\pi D}\, r_0^2 \sqrt{t}\right] \qquad (6)$$

where D is the sum of the diffusion coefficients of the reactants, c' is the concentration of quencher (oxygen in this case), and r_0 is the donor-acceptor encounter distance. In order that our results can be described by Eq. (6), during the whole decay the second term in the exponent should be much bigger than the first one. To fulfill this condition, the experimental results yield physically meaningless values for r_0 and D, either considering our results or the ones of Draxler et al. Furthermore, taking into account that the values of the diffusion coefficient and the permeability of oxygen in PDMS are sufficiently high ($3.7 \times 10^{-5}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ and $4 \times 10^{-11}\,\mathrm{cm}^3(\mathrm{STP})\,\mathrm{cm}^{-1}\,\mathrm{s}^{-1}\,\mathrm{Pa}^{-1}$, respectively [4]), steady state for diffusion should be prevalent in the μs timescale of the Ru complexes luminescence decay.

The conclusion of this kinetic analysis is that oxygen quenching should be homogeneous as oxygen is mobile enough in the polymer. Therefore, the drop in the efficiency of the luminescence quenching should reflect that the oxygen concentration in the polymer is not linear with P_{O_2}. Furthermore, the Stern–Volmer relation is a direct measure of the oxygen concentration in the polymer, $[O_2]_p$, as expressed by Eq. (7):

$$\frac{I_{f_0}}{I_f} = 1 + K_{SV}[O_2]_p \qquad (7)$$

Our results can be explained on the basis of a domain model [15]. We have a hydrophobic domain, PDMS, and also a phase heterogeneity due to the presence of the dopant of E4 commercial silicone. In our system, the dopant particles represent domains on which the complex can be adsorbed. The polymer acts as a protective and oxygen permeable layer that overlays the solid surfaces. If we suppose the complex is adsorbed, the oxygen quenching results can be treated by considering surface quenching by adsorbed oxygen.

A Langmuir type dependence of $[O_2]_p$ is found in polymers below the glass-rubber transition temperature, Tg [30]. PDMS is above the Tg at room temperature. Nevertheless, Langmuir sorption isotherms for gases are found for doped polymers [31] as is the commercial source of PDMS used to build the sensors. For this reason, we tried to fit $[O_2]_p$ by a Langmuir isotherm, transforming Eq. (7) to:

$$\frac{I_{f_0}}{I_f} - 1 = \frac{a P_{O_2}}{1 + b P_{O_2}} \qquad (8)$$

where a and b are adjustable parameters. The constant a is the product of a concentration factor, describing the saturation of the polymer with oxygen, and the Stern–Volmer constant, taking into account the efficiency of quenching by oxygen. The constant b represents the inverse pressure at which oxygen is at half its saturation concentration. While a should depend on the polymer and the probe, b should depend only on the polymer. When the results of Fig. 2

are adjusted to Eq. (8), the value of b for Ru(dpp)$_3$ is more than six times bigger than the value for Ru(phen)$_3$. This is in disagreement with the prediction as the two complexes are exposed to the same oxygen concentration in the polymer at the same P_{O_2}.

In some cases, systems with polar dopants were found to obey a Freundlich adsoption isotherm [14].

$$[O_2]_p = K_f P_{O_2}^{1/n} \quad (9)$$

where $n > 1$, is a parameter related to the intensity of the adsorption and K_f indicates the $[O_2]_p$ when the pressure is unity.

When this dependence of $[O_2]_p$ on P_{O_2} is taken into account, Eq. (7) can be written as:

$$\frac{I_{f0}}{I_f} - 1 = K_{SV} K_f P_{O_2}^{1/n} = K_t P_{O_2}^{1/n} \quad (10)$$

The data are plotted in the logarithmic form of Eq. (10) in Fig. 5. In spite of the difference in quenching ability between Ru(phen)$_3$ and Ru(dpp)$_3$, the two straight lines are parallel reflecting the same value of 1/n, and thus common adsorption characteristics. The other constant of the fit is K_t, that contains the product of three parameters: (i) the quenching rate constant of the excited state by O$_2$, (ii) a characteristic time for the excited state in the absence of O$_2$, and (iii) the constant K_f of the Freundlich isotherm. This later factor should be the same for both complexes as it reflects O$_2$ adsorption characteristics in the polymer matrix. The quenching rate constant of the excited state by O$_2$ should be approximately the same for both complexes as it is a diffusion controlled process. The characteristic time for the excited state in the absence of O$_2$, can be taken as the average time of the decay, $\langle t \rangle$, since the kinetics is not monoexponential. From Eq. (2), $\langle t \rangle = 6/B^2$ is obtained. Considering the previous discussion, the ratio of K_t for the two complexes should equal the ratio of $\langle t \rangle$ in the absence of O$_2$. From Fig. 4 we obtain $B = 2020\ s^{-1/2}$ for Ru(phen)$_3$, and $B = 1200\ s^{-1/2}$ for Ru(dpp)$_3$ in the absence of O$_2$. This gives a ratio of 0.35 for $\langle t \rangle$ of Ru(phen)$_3$ compared to Ru(dpp)$_3$. The ratio of the respective K_t (see fitting parameters in Fig. 5) is 0.18. The coincidence of the order of magnitude can be considered satisfactory when it is noted that the previous discussion does not take into account the microheterogeneous character of the sample.

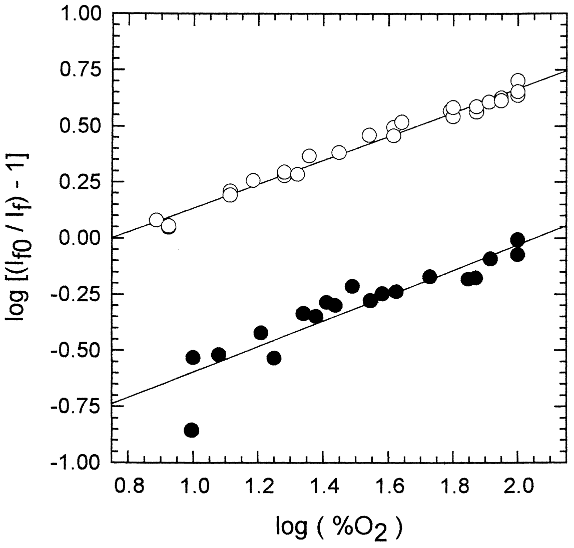

Fig. 5. Logarithmic plot of the luminescence intensity as a function of oxygen pressure. The lines are the best fits according to Eq. (10): (●) Ru(phen)$_3$, with $K_t = 0.070 \pm 0.014$, and $(1/n) = 0.57 \pm 0.06$; (○) Ru(dpp)$_3$, with $K_t = 0.40 \pm 0.02$ and $(1/n) = 0.53 \pm 0.01$.

The steady-state luminescence data of Draxler et al. for Ru(dpp)$_3$ in silicone E4 (from [17], Fig. 1), were treated in the same way, yielding $1/n = 0.65$, very near the values obtained in our system.

In conclusion we can say that the adsorption model applied for this system describes very well the excited state quenching by oxygen and its dependence on P_{O_2}. The departure of the kinetics from a monoexponential behaviour is due to the microheterogeneity of the system, and it seems to vary greatly in the different matrixes. In this respect, the stretched exponential law proved to describe the decays in a precise way in many similar cases, though it provides no physical information of the reasons of the microheterogeneity.

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