Mechanism of oxygen-induced EPR line broadening in lithium phthalocyanine microcrystals

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Abstract

EPR oximetry has been recognized as an important tool for determining oxygen concentration in biological tissues, in vivo. The method relies on the use of oxygen-sensitive paramagnetic probes whose linewidth varies predictably, mostly linear, with oxygen concentration. Lithium phthalocyanine (LiPc) radical has emerged as the probe of choice due to its superior EPR sensitivity, oxygen response, and biocompatibility. However, there are certain limitations in the preparation of this material in a pure and usable form. In our efforts to improve the synthesis of this material for reliable use in oximetry applications, we developed microcrystalline particulates that showed several advantages over other probes. Despite its advantages, the probe shows linear response to pO_2 only in the range of 0–70 mmHg, beyond which a saturation behavior is observed. The goal of this study was to understand the mechanism of the interaction of oxygen with LiPc in order to interpret the experimentally observed linewidths. We propose a dual-spin model in which the freely diffusing spins of LiPc are converted to fixed spins by adsorption of molecular oxygen. The proposed mechanism was verified from the effect of oxygenation/deoxygenation processes on the linewidth of LiPc. In summary, we demonstrated that adsorption of oxygen molecules on LiPc contributes to a nonlinear line-broadening effect. This understanding is important for the future design of new EPR oximetry probes.
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1. Introduction

Lithium phthalocyanine (LiPc) is one of the most widely studied organo-metallic compounds due to its unique magnetic and electrical properties [1–3]. It exhibits three distinct crystalline polymorphs, designated as α-, β-, and x-form, whose structural, magnetic, and electrical properties have been well characterized in single crystals [3], powders [1], and thin films [4]. The crystals are composed of stacks of neutral radicals of LiPc molecules with strong exchange-coupling between the unpaired electron spins. The electron paramagnetic resonance (EPR) properties of LiPc are of particular interest for several reasons. LiPc exhibits a single and narrow-line EPR spectrum and its spectral-width is highly sensitive to the concentration of the surrounding molecular oxygen [5]. The effect of molecular oxygen on the EPR lineshape of LiPc triggered the application of this material as a probe for measurement of oxygen concentration (oximetry) in biological systems [6]. The EPR oximetry is based on the Heisenberg spin exchange between paramagnetic oxygen and LiPc which results in shortening of the life-time of LiPc spins in the excited state (T_2^* relaxation). The effect is observable in the form of changes in the linewidth of its EPR spectrum. Of the three known polymorphs of LiPc, only the x-form undergoes Heisenberg spin exchange with molecular oxygen and hence is useful for EPR oximetry [1,6]. The other two forms are also paramagnetic and, although not oxygen-sensitive, their presence can interfere with the EPR measurement of the x-form. However, the preparation of the x-form in a pure form had been difficult [7]. Recently, we reported a reliable

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electrochemical procedure for the preparation of the x-form of LiPc and demonstrated its use as an oximetry probe in a variety of in vitro and in vivo biological studies [8,9]. An advantage of this procedure is that the LiPc is synthesized in the form of microcrystalline needles of 10–60 μm long, which is more stable in the tissues compared to larger single crystals [6]. The size of the crystals can be further reduced to 0.2–0.5 μm by sonication in aqueous suspensions.

We observed some striking differences in the effect of molecular oxygen on the EPR lineshape of the LiPc microcrystals, which we have prepared, compared to that in single crystals of LiPc reported by others [6]. Unlike many soluble probes and some particulate probes that show linear dependence of their EPR linewidth with concentration of molecular oxygen (pO_2), the LiPc microcrystals show significant nonlinear dependence of its linewidth [10]. For example, while a linear response of linewidth to oxygen was observed in single crystals of LiPc [6], fusinite [11], nitroxides [12], or trityl [13] for up to 100% (760 mmHg) of oxygen concentration at ambient pressure, the microcrystalline form of LiPc showed linearity only in the range of 0–10% oxygen [10]. This indicated that the broadening mechanism in the case of LiPc microcrystals at higher oxygen concentrations might be dominated by processes other than Heisenberg spin exchange between oxygen and LiPc. We further observed that both the range of linearity and sensitivity (slope of the linewidth versus pO_2 curve in the linear region) of the LiPc were dependent on the size of the crystals [10]. The particle size-dependent sensitivity was interpreted as due to the occurrence of Knudson diffusion of oxygen in the microchannels of LiPc. The Knudson diffusion predicts that the oxygen flux in the channels is inversely related to the size of the microcrystals. The interpretation of nonlinearity (saturation) in the linewidth versus pO_2 curve was explained based on the concept of 'dual-spins,' namely, diffusing spins and fixed spins [10]. We reported that the conversion of the diffusing (fast-exchange) spins in LiPc into fixed spins by molecular oxygen could contribute to the saturation of line broadening at higher concentrations of oxygen. However, the mechanism by which this conversion could occur was not established, although we had speculated that adsorption of oxygen on LiPc might be responsible for this conversion [10].

Recently, Kanemoto and Yamauchi [14] reported a similar saturation behavior in the EPR linewidth of polypyrrole (PPy) as function of oxygen concentration and established that adsorption of oxygen in the micropores of PPy was responsible for the saturation behavior. They had used Langmuir adsorption isotherm model in conjunction with EPR data to establish their conclusions. As PPy and LiPc exhibit similar characteristics in terms of spin diffusion in the host lattice and

oxygen-induced effects on the EPR spectra, we used the Langmuir adsorption isotherm model in combination with the dual-spins concept to interpret the oxygen-induced line broadening in the EPR spectra of LiPc microcrystalline powder. We hypothesized that a careful analysis of the EPR data in the light of the proposed adsorption and dual-spin models should provide important insights into the mechanism of the interaction of oxygen with LiPc and that it would be useful for the design of new probes for oximetry applications. Our results establish that adsorption of oxygen molecules on LiPc contributes to the saturation of the EPR line broadening at higher oxygen concentrations.

2. Experimental

2.1. Synthesis of LiPc microcrystals

Lithium phthalocyanine was synthesized by a constant-potential electrolysis method under continuous stirring [8]. The procedure is known to yield fine crystals of the x-form. The crystalline nature of the material was established by X-ray powder diffraction [8]. The needle-shaped crystals were 10–60 μm in length.

2.2. EPR measurements

EPR measurements were carried out using a 9.78 GHz (X-band) Bruker ER 300 spectrometer. Data acquisition and analysis were performed using a Personal Computer (PC) interfaced to the spectrometer. Instrument control, data acquisition, and data processing were performed using software developed in the laboratory. Low modulation amplitudes (<10 mG), at a modulation frequency of 12.5 kHz, were used to avoid any distortion to the spectral lineshape [15]. Also, the measurements were performed under nonsaturating incident microwave powers, 20–50 μW. A calibration curve of EPR linewidth versus pO_2 was constructed from X-band EPR measurements on LiPc equilibrated with known ratios of oxygen/nitrogen gas mixture, as reported previously [9].

3. Results and discussion

3.1. Effect of molecular oxygen on the EPR linewidth of LiPc

The EPR spectrum of LiPc microcrystalline powder showed a single peak with a peak-to-peak linewidth of ∼20 mG under anoxic conditions (equilibrated with 100% nitrogen gas at ambient pressure). The linewidth increased as a function of pO_2 of the equilibrating gas,
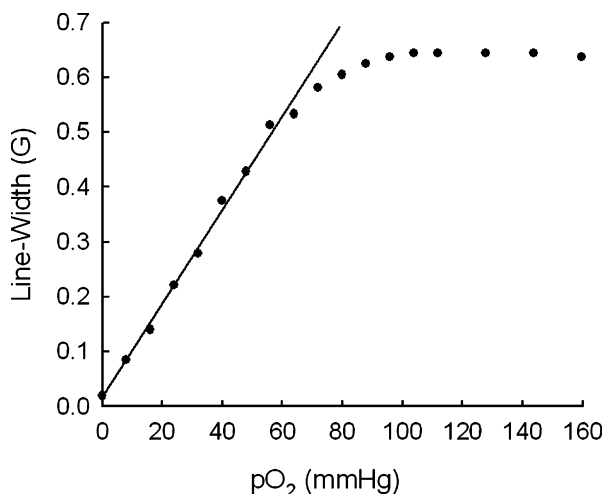
Fig. 1. Effect of pO_2 on the EPR linewidth (peak-to-peak) of LiPc microcrystalline powder. The measurements were performed at X-band (9.78 GHz). The data show a linear response up to 70 mmHg, beyond which a nonlinear response is observed.

as shown in Fig. 1. The linewidth was proportional to pO_2 and increased linearly with increase in pO_2 in the range 0–70 mmHg, but showed saturation at higher pO_2 values. In general, spin systems subjected to Heisenberg exchange show linear variation of linewidth with pO_2. The nonlinear variation of linewidth with pO_2 in LiPc suggests that there may be additional mechanism(s) which may become significant at the higher oxygen concentrations.

3.2. Dual-spin model for LiPc in presence of oxygen

The mechanism of EPR line broadening in LiPc in the presence of O_2 can be explained based on a dual-spin model similar to that proposed by Holczer et al. [16] and Nechtschein et al. [17] for *trans*-polyacetylene systems. In the dual-spin model, there are two types of spins: (i) diffusing spins that move along the stack axis of crystal and (ii) fixed spins that reside at definite locations. Molecular oxygen, by residing in the proximity of LiPc spins, behaves as a trap and converts diffusing spins into fixed spins. Since the interplanar distance in LiPc crystal is less than van der Walls radii [3,8], strong Heisenberg spin exchange interaction exists between the neighboring molecules through antiferromagnetic coupling. This results in spin diffusion along the stack axis of crystals leading to very narrow EPR line. We have previously shown using low temperature measurements that the spin diffusion is prevented at low temperatures and subsequently the EPR linewidth is increased, similar to the effect of oxygen [10]. The existence of spin diffusion and two types of spins in LiPc is evidenced by the following observations. The EPR spectral intensities obtained at two different temperatures under anoxic conditions are shown in Fig. 2A. The higher intensity
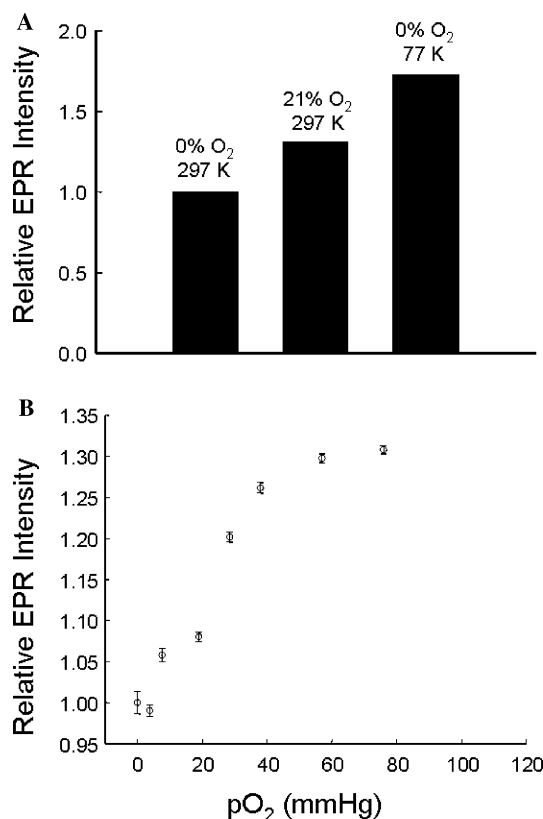

Fig. 2. (A) EPR spectral intensity obtained at room temperature (RT, 297 K) and at liquid nitrogen temperature (LNT, 77 K). (B) Spectral intensity (obtained from double integration of the first derivative spectra) as a function of pO_2.

seen at 77 K is due to the removal of spin diffusion and arresting of the diffusing spins [10]. In addition, the intensity of the spectrum increased with pO_2 (Fig. 2B). In a normal Heisenberg spin exchange mechanism involving spin probe and molecular oxygen (as typically observed between a nitroxide and oxygen in solution), the EPR linewidth increases while the area under the EPR spectrum remains unchanged. The increased spectral intensity of LiPc observed in the present work is due to the arrest of antiferromagnetic coupling of the diffusing spins and conversion to fixed spins.

Under anoxic conditions, there are no oxygen traps and hence the LiPc spins are diffusing freely along the stack axis with a spin diffusion frequency, f_{hop}, resulting in the narrowest EPR spectrum. When oxygen is introduced the oxygen molecules trap the diffusing spins and convert them into fixed spins. Since there are two different populations of spins, diffusing spins and fixed spins at any given pO_2, there should be two EPR lines, a narrow line corresponding to the diffusing spins and a broad line corresponding to the fixed spins. However, only one EPR line is observed in LiPc at all oxygen concentrations. The appearance of a single line is attributed to the fast switching frequency (f_{swi}) between the two types of spins [18,19]. That is, the spins are in-

distinguishable at the time-scale of EPR spectroscopy. The existence of two types of pools of spins, but with a single EPR line has been postulated by Holczer et al. [16] and Nechtschein et al. [17] in *trans*-polyacetylene systems. Alternatively, Atsarkin et al. [20] have observed a similar saturation in the linewidth versus pO_2 plot of carbon chars. The data were interpreted based on the consideration of two different spin sites, namely, bulk sites and surface sites with spin exchange between them. However, two distinct EPR spectra were observed due to incomplete averaging between the sites [20].

3.3. Adsorption of oxygen on LiPc

When LiPc crystals are exposed to gaseous oxygen, the oxygen molecules can interact with LiPc spins by collision or by adsorption on the LiPc lattice. The former interaction will induce relaxation (T_2) of the excited spin state of LiPc resulting in broadening of the absorption with a linear dependence of linewidth on pO_2. On the other hand, if oxygen is adsorbed, then saturation in the surface coverage will occur at higher pO_2 values. The saturation of line broadening by oxygen at higher pO_2 values can be interpreted on the basis of the dual-spin model of LiPc spins. A schematic illustration of the conversion of diffusing spins to fixed spins in LiPc lattice is shown in Fig. 3. It is assumed that oxygen molecules are adsorbed on specific sites in the lattice and that the number of such sites is fixed in a given lattice. An oxygen molecule that is adsorbed in the proximity of an LiPc spin will convert it to a fixed spin. According to this model, the population of fixed spins (Fig. 3) can

vary from zero, in the absence of oxygen, to the maximum available sites in LiPc. Under these circumstances, at lower pO_2 values the number of fixed spins and adsorbed oxygen will increase proportionately with increase in pO_2. However, at higher pO_2 values the process will show saturation due to saturation of the readily available sites for adsorption. Thus the population of fixed spins will soon reach a limit, beyond which oxygen will not have any effect.

Evidence for specific adsorption of oxygen on LiPc was obtained from the following gas-exchange EPR experiment. The EPR response of LiPc was continuously measured, by fixing the magnetic field corresponding to the peak of LiPc under anoxic condition, while the equilibrating gas (maintained at a flow rate of 2 L/min) was rapidly switched from nitrogen to room air and vice versa. As shown in Fig. 4, the absorption at deoxygenated condition rapidly decreased on introduction of oxygen due to line broadening. The time required to reach equilibrium with room-air oxygen was 1.5 s. However, when the equilibrating gas was switched to nitrogen it took more than 15 s to return to the level of original absorption at anoxic condition. The experiment revealed two important characteristics of deoxygenation: (i) the recovery of the original anoxic absorption after re-equilibration with nitrogen gas shows that the total spin density of LiPc is intact and that there is no chemical oxidation of LiPc by oxygen, and (ii) the longer period required to restore the anoxic linewidth, which is apparently the time required for the complete removal of oxygen, indicates that oxygen has certain affinity toward the LiPc lattice. The gas-exchange
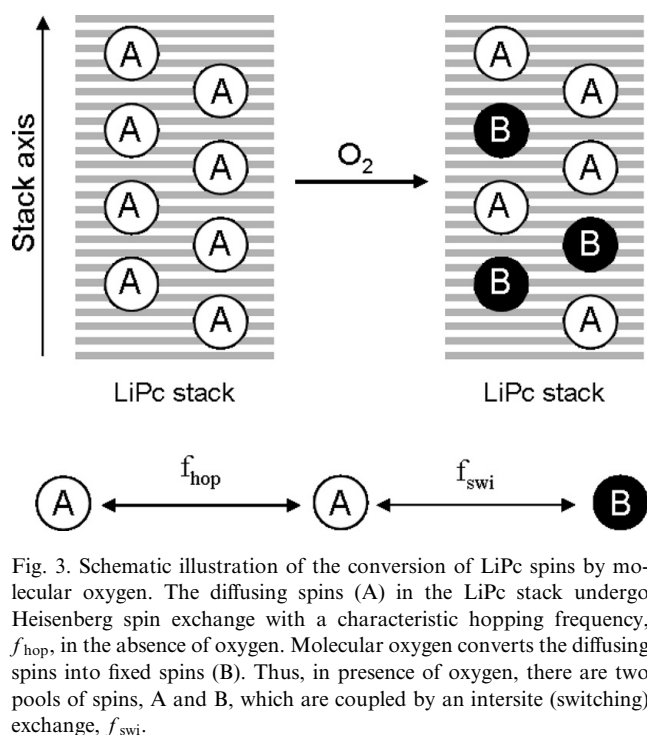

Fig. 3. Schematic illustration of the conversion of LiPc spins by molecular oxygen. The diffusing spins (A) in the LiPc stack undergo Heisenberg spin exchange with a characteristic hopping frequency, f_{hop}, in the absence of oxygen. Molecular oxygen converts the diffusing spins into fixed spins (B). Thus, in presence of oxygen, there are two pools of spins, A and B, which are coupled by an intersite (switching) exchange, f_{swi}.
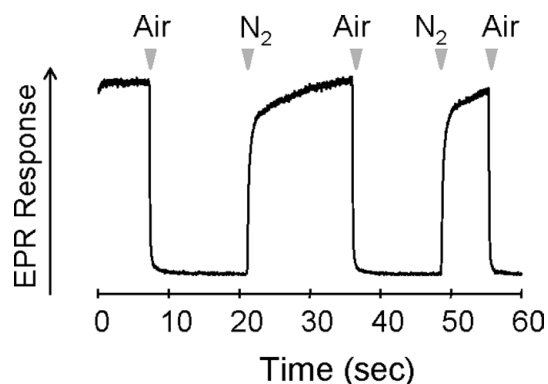

Fig. 4. Effect of oxygenation/deoxygenation on the EPR response signal of LiPc. The magnetic field was set at the peak of the spectrum under nitrogen equilibration and the response of was monitored as a function of time during fast gas-switching. Room air ($\sim$21% O_2) and Nitrogen (100% N_2) were repeatedly switched as indicated. When the N_2-saturated LiPc was exposed to air the intensity changed in <1 s. Similarly when the gas was switched to 100% N_2, an immediate increase in the intensity was observed. However, the deoxygenation process was slower and took more than 15 s to recover completely. The process was highly reversible, suggesting that there was no permanent absorption of oxygen.

experiments indicate that the nature of binding of oxygen to LiPc is likely to be physical adsorption. To verify that the slow response during deoxygenation was not due to out-gassing from the apparatus, we performed the deoxygenation experiments with two other materials, namely, lithium naphthalocyanine [21] and lithium octa-n-butoxy-naphthalocyanine [22], under identical conditions. We observed that the deoxygenation kinetics of these materials were significantly different from that of LiPc suggesting that the observed difference in the deoxygenation kinetics is fundamental to LiPc and not due to out-gassing of oxygen from the apparatus. Further attempts to study the adsorption/desorption phenomena of oxygen in LiPc by variable temperature measurements were unsuccessful, because the variation in temperature not only affects the adsorption/desorption kinetics of O_2 in the LiPc lattice, but it also affects the intrinsic linewidth of LiPc [10].

3.4. A gas-phase adsorption model

The adsorption characteristics of oxygen on LiPc can be obtained from the EPR line broadening data and analysis of the adsorption isotherm (the pO_2 versus linewidth curve) using the approach reported for PPy [14]. As considered in the case of PPy, molecular O_2 is presumed to penetrate into the LiPc bulk volume and thus the phenomenon is a sort of solution of O_2 inside the LiPc lattice. Hence, it can be assumed that with the increase in pO_2 the amount of adsorbed O_2 inside the bulk increases. The surface coverage, θ, defined as the ratio of number of sites occupied by O_2 (N_a) to the total number of sites available (N), is increased as a function of pO_2. Thus it is possible to evaluate the adsorption parameters from the linewidth–pO_2 relationship. Assuming that there is no interaction between the adsorbed O_2 molecules, a simple Langmuir adsorption isotherm (with the assumption of monolayer surface coverage by O_2 and homogeneous adsorption energetics of the adsorption sites) can be used. The rate equation for θ is given as [14]

$$d\theta/dt = k_a pO_2(1 - \theta) - k_d\theta, \qquad (1)$$

where k_a and k_d are the rate constants of adsorption and desorption, respectively. Solving for θ at equilibrium, we obtain

$$\theta_{eq} = KpO_2/(1 + KpO_2), \quad \text{where } K = k_a/k_d. \qquad (2)$$

The surface coverage θ_{eq} can be expressed in terms of the observed EPR linewidth (ΔB_{O_2}) as

$$\theta_{eq} = (\Delta B_{O_2} - \Delta B_0)/(\Delta B_\infty - \Delta B_0), \qquad (3)$$

where ΔB_0 and ΔB_∞ are the widths at anoxic and at maximum adsorptive state, respectively.

By combining Eqs. (2) and (3) and rearranging, we obtain,

$$pO_2 = [(\Delta B_\infty - \Delta B_0)/(\Delta B_{O_2} - \Delta B_0)]pO_2 - 1/K. \qquad (4)$$

The above equation is a form of adsorption isotherm. A plot of pO_2 versus $pO_2/(\Delta B_{O_2} - \Delta B_0)$ is expected to be linear with slope $(\Delta B_\infty - \Delta B_0)$ and intercept $1/K$. The experimental data plotted as per Eq. (4) is shown in Fig. 5. The x-axis represents the amount of oxygen (in mmHg) necessary to cause a broadening of 1 mG at a given pressure of oxygen in the y-axis. If there were no saturation, the amount of oxygen necessary to cause a unit broadening should be constant at all concentrations of oxygen. The vertical line in Fig. 5 (inset) at $x = 0.12$ mmHg/mG corresponds to the linear portion of the linewidth versus pO_2 plot shown in Fig. 1. The non-vertical nature of the curve in Fig. 5 clearly demonstrates the presence of a nonlinear effect or saturation. Linearity of the plot in the pO_2 range 70–760 mmHg demonstrates the validity of the adsorption model. The results show that the adsorption-mediated broadening dominates only in the higher pO_2 range while the homogeneous broadening (spin exchange between oxygen and LiPc) is dominant in the lower pO_2 range.

Based on the linear portion of the plot in Fig. 5, we determined the following adsorption parameters: $\Delta B_\infty = 680$ mG; $K = 0.042$ mmHg^{-1}; $\theta = 87\%$ at room air and ambient pressure. The surface coverage (θ) was high compared to 40% surface coverage reported for PPy [14]. The high surface coverage at ambient pressure explains why the linewidth versus pO_2 curve gets saturated at very low pO_2 (about 100 mmHg) in LiPc, whereas in the case of PPy saturation is not reached even at 760 mmHg. The results indicate that the LiPc microcrystalline powder has a high degree of affinity towards adsorption of oxygen.
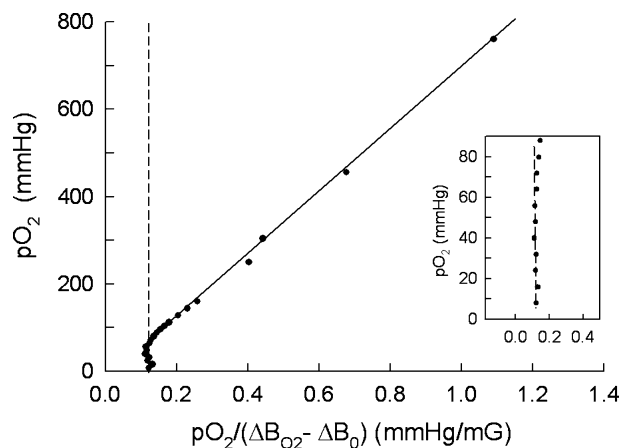

Fig. 5. Plot of pO_2 versus $pO_2/(\Delta B_{O_2} - \Delta B_0)$. The total pressure was maintained constant at 760 mmHg. The vertical line at $pO_2/(\Delta B_{O_2} - \Delta B_0) = 0.12$ mmHg/mG (also shown in the inset) corresponds to the linear portion of the linewidth versus pO_2 plot shown in Fig. 1. From the slope of the linear region, the ΔB_∞ and K (cf. Eq. (2)) were determined to be 680 mG and 0.042 mmHg^{-1}, respectively.

4. Conclusions

The present results indicate that the EPR line broadening of LiPc microcrystalline powder by O_2 is suggestive of a dual-spin mechanism and that the saturation behavior, observed in the EPR linewidth versus pO_2 curve at $pO_2 > 70$ mmHg, is due to reversible adsorption of oxygen molecules. It should be noted that the x-form of LiPc that we have used in the present study is known to have channels of 5.9 Å diameter [23], which is just wide enough for the oxygen molecules (size: 2.8×3.9 Å) to get through. The exact nature of the sites wherein the oxygen molecules are trapped is not known. Considering that the interplanar spacing between the LiPc molecules are not large enough for oxygen to diffuse through, it is quite reasonable to expect that the oxygen molecules may be adsorbed at defective locations in the channel. This expectation is supported by the fact that the LiPc microcrystals were crystallized under constant stirring conditions which might induce the formation of defective sites (strain) in the lattice. On the contrary, the LiPc material synthesized under non-stirring conditions is reported to yield large single crystals (up to 200 μm) with significantly reduced or negligible saturation in the line broadening properties [6]. Furthermore, we did not observe the saturation behavior in lithium naphthalocyanine crystals where the channel sizes are much larger (8.1–9.0 Å) [21,22,24]. Thus, it seems very likely that the presence of tight channels and possible defect structures in the channels of the microcrystals of LiPc are responsible for the observed saturation phenomenon. Further work is in progress to delineate the particle size-dependent changes in the exchange and oximetry properties of these crystals.

Acknowledgments

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