

# Temperature Dependence of Pressure Sensitive Paints

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The photoluminescence properties of a typical pressure sensitive paint (PSP) formulation consisting of tris-(4,7-diphenylphenanthroline)ruthenium(II) dichloride (RudpCl) dispersed in a polydimethylsiloxane (PDMS) binder were examined as a function of temperature. Thus, the temperature dependence of the luminescence intensity  $I_{em}$  and emission decay lifetime  $\tau_{em}$  of the PSP formulation and for the photoluminescent RudpCl dye dissolved in ethanol solvent were determined for temperatures ranging from 5 to 50°C. Analysis of the experimental data indicates that under deoxygenated conditions the temperature dependence of  $I_{em}$  and  $\tau_{em}$  for either the PSP formulation or ethanol solutions is dominated by the intrinsic temperature dependence of the nonradiative decay rate of the photoluminescent dye molecule. By contrast, for the PSP formulation at 1-atm air pressure the temperature dependence of  $I_{em}$  and  $\tau_{em}$  is dominated by the temperature dependence of the diffusivity of oxygen in the PDMS binder. The implications of the experimental results on the design and application of PSP formulations are discussed.

## Nomenclature

$A$	= preexponential frequency factor
$C$	= constant
$D$	= mass diffusivity
$E$	= activation energy
$I_{em}$	= luminescence emission intensity
$K_{SV}$	= Stern–Volmer constant
$k$	= luminescence decay rate constant
$[O_2]$	= oxygen concentration
$R$	= gas constant (1.987 cal/mole K)
$T$	= temperature
$t$	= time
$\alpha_1, \alpha_2, \alpha_3$	= amplitude factor for Eq. (6)
$\beta$	= temperature sensitivity term
$\lambda$	= wavelength
$\tau, \tau_{em}$	= luminescence emission decay lifetime
$\langle \tau \rangle$	= weighted average lifetime; Eq. (7)
$\Phi_{em}$	= luminescence emission quantum efficiency

## Subscripts

atm	= atmospheric condition
nr	= nonradiative
$q$	= quenching
$r$	= radiative

## Superscripts

0	= vacuum
1 atm	= value taken at 1-atm pressure

## I. Introduction

**P**RESSURE sensitive paints (PSP) are gaining wide acceptance as an accurate and cost-effective full field surface pressure mea-

surement technique.<sup>1,2</sup> Originally applied in supersonic and transonic flows with large pressure gradients, the technique is successfully being applied in low-speed flows<sup>3</sup> and to rotating machinery.<sup>4</sup> Major difficulties with the technique include corrections for model movement,<sup>5,6</sup> limited time response,<sup>7</sup> and temperature effects.<sup>1,2</sup> The latter effect is currently one of the major factors that limits the accuracy available in application of PSP to full field surface pressure measurement.

The dyes used in PSP formulations are inherently sensitive to temperature changes as well as to changes in the concentration of oxygen within the coating. Although the temperature dependence of the PSP can be used to advantage (i.e., for full field temperature measurements), it is a large source of error for pressure sensing applications.<sup>1,2,8,9</sup> This paper presents the results and analysis of an experimental investigation that explored the origins of the temperature dependence of a typical PSP formulation comprising a luminescent polypyridine Ru(II) complex dispersed within a polydimethylsiloxane (PDMS) binder. The results of this investigation reveal that the temperature dependence of the luminescence from the PDMS-based PSP system originates from two terms. The smallest component arises from the intrinsic temperature dependence of the (thermally activated) nonradiative decay channel of the luminescent Ru(II) dye, whereas the dominant term is due to the temperature dependence of the diffusivity of molecular oxygen within the PDMS binder. These results are important in guiding the development of new PSP formulations with improved temperature sensitivities and in developing temperature compensation methods.

## II. Materials, Methods, and Instrumentation

The PSP formulation used herein comprised tris-(4,7-diphenylphenanthroline)-Ru(II) dichloride (RudpCl) dissolved in a PDMS binder. RudpCl was synthesized by a literature procedure and purified by repeated recrystallization from water.<sup>10</sup> The silicone binder was derived from diacetoxycapped PDMS (Gelest, Inc., DMS-D33). In a typical film preparation, 3.0 mg of RudpCl and 1.0 g of PDMS were dissolved in 4 ml of dichloromethane. The resulting solution was spray coated onto several borosilicate glass slides by using a commercially available air brush. The coated slides were then allowed to dry for 24–48 h at ambient temperature. Under conditions of low humidity, the RudpCl/PDMS films typically dried completely within 48 h; however, if the humidity was high, the films remained tacky even several days after spray coating. Only films that were dry to the touch (i.e., not tacky) were used for luminescence studies. Comparisons between the luminescence properties of the RudpCl/PDMS films and RudpCl/ethanol solutions were performed. The solutions were prepared using reagent grade

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absolute ethanol, and the concentration of RudpCl was  $5 \times 10^{-5}$  M (mole/liter). Steady-state emission studies were carried out on a commercially available fluorescence spectrophotometer (SPEX Industries, F-112A). Time resolved emission studies were carried out by time correlated single photon counting on a commercially available instrument (Photochemical Research Associates, FLI). Luminescence decays were analyzed by using the DECAN software package.<sup>11</sup>

Emission lifetimes for RudpCl dissolved in ethanol were determined for solutions at equilibrium with 1-atm air pressure and for solutions that were thoroughly degassed by bubbling with argon. Emission lifetimes of RudpCl dispersed in PDMS films were obtained for samples at equilibrium with 1-atm air pressure and for samples that were maintained under high vacuum (pressure  $< 2 \times 10^{-4}$  atm). Liquid and film samples were affixed in custom-built sample holders that could be maintained at constant temperature by means of a temperature controlled recirculating water bath. Experimental data represent results of a variable temperature run on a single sample. However, all temperature dependence experiments were repeated at least three times on independently prepared samples to confirm that the results were reproducible.

### III. Background: Molecular Photophysics

To understand the experimental approach that was the heart of this study, it is necessary to briefly outline pertinent background material on molecular photophysics. The presentation herein is brief; more detailed discussions are available in the literature.<sup>12–17</sup>

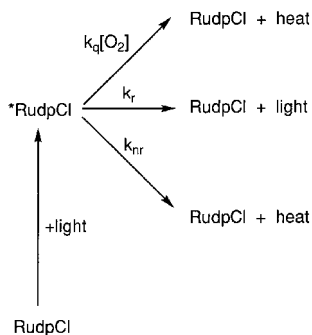
Photoexcitation of the RudpCl dye in the blue region of the visible spectrum produces the luminescent molecular excited state, \*RudpCl. In the presence of oxygen, \*RudpCl has available three decay channels, which operate in parallel (Fig. 1): 1) emission of a photon (radiative decay) with first-order rate constant  $k_r$ ; 2) transfer of thermal energy to the surrounding medium (nonradiative decay) with first-order rate constant  $k_{nr}$ ; and 3) quenching by interaction with molecular oxygen with pseudo-first-order rate  $k_q[O_2]$ , where  $[O_2]$  is the oxygen concentration and  $k_q$  is the second-order rate constant for the quenching process. For a luminescent molecule such as RudpCl, it is possible in principle to experimentally determine the luminescence quantum efficiency  $\Phi_{em}$  and the emission decay lifetime  $\tau_{em}$ . In practice, however, the former term is very difficult to determine for specimens comprising a dye dispersed in a solid film; thus, for the present studies we will refer to the luminescence intensity  $I_{em}$ , which is proportional to the quantum efficiency (i.e.,  $I_{em} = C\Phi_{em}$ , where  $C$  is a constant). These experimentally accessible parameters are related to the rate constants of the individual decay channels by the following expressions:

$$I_{em} = \frac{Ck_r}{k_r + k_{nr} + k_q[O_2]} \quad (1)$$

$$1/\tau_{em} = k_r + k_{nr} + k_q[O_2] \quad (2)$$

When a vacuum is imposed (or the sample is degassed with an inert gas, i.e., argon), the oxygen concentration in the sample vanishes and the natural emission decay lifetime  $\tau_{em}^0$  is related to  $k_r$  and  $k_{nr}$  as follows:

$$1/\tau_{em}^0 = k_r + k_{nr} \quad (3)$$



**Fig. 1** Diagram illustrating decay pathways available to photochemically excited RudpCl.

Dividing Eq. (1) by Eq. (2) yields

$$I_{em}/\tau_{em} = Ck_r \quad (4)$$

which reveals that the emission intensity-lifetime ratio is proportional to the radiative decay rate  $k_r$ .

For a sample consisting of a dilute homogeneous solution of luminescent dye in a fluid solvent (i.e., RudpCl in ethanol), pulsed excitation produces emission that decays according to a single exponential expression, i.e.,

$$I_{em}(t) = I_{em}^0 \exp(-t/\tau_{em}) \quad (5)$$

where  $t$  is time. An exponential emission decay is observed because the instantaneous emission intensity is directly proportional to the concentration of \*RudpCl, and, as indicated by Fig. 1, \*RudpCl decays according to a first-order kinetic law. By contrast, the emission of RudpCl dispersed in PDMS films does not decay according to Eq. (5). Thus, to adequately simulate the emission decays, an expression consisting of a sum of three exponential terms is required:

$$I_{em}(t) = \alpha_1 \exp(-t/\tau_1) + \alpha_2 \exp(-t/\tau_2) + \alpha_3 \exp(-t/\tau_3) \quad (6)$$

where  $\alpha_i$  and  $\tau_i$  are, respectively, the amplitude and lifetime of the  $i$ th exponential decay component.

Multieponential emission decays are typically observed for molecules dissolved in polymer films or in frozen solvent glasses.<sup>18</sup> The basis for the multieponential behavior is that the luminescent dye molecules are in an inhomogeneous environment in the solid medium. The inhomogeneity is associated with the fact that the host matrix has domains that vary with respect to their interaction with the luminescent probe. As a result, there is a dispersion in the rates for each of the three decay channels of the molecules. In effect, some molecules decay more rapidly than others because of their different environments. It is likely that the inhomogeneity influences primarily  $k_{nr}$ ; however, some dispersion in  $k_r$  and  $k_q[O_2]$  is also to be expected.

To simplify the analysis of the temperature dependent emission decay data for the RudpCl/PDMS films, we have used the three exponential fits of the experimental emission decay data to calculate the median lifetime  $\langle\tau\rangle$ , which is defined by the following equation:

$$\langle\tau\rangle = \frac{\alpha_1 \tau_1 + \alpha_2 \tau_2 + \alpha_3 \tau_3}{\alpha_1 + \alpha_2 + \alpha_3} \quad (7)$$

where  $\alpha_i$  and  $\tau_i$  are, respectively, the amplitude and lifetime of the  $i$ th exponential decay component obtained from fits of the experimental decay data according to Eq. (6).

### IV. Experimental Results

The RudpCl/PDMS system comprises a typical PSP formulation.<sup>19</sup> The dye is excited with blue light ( $\lambda_{ex} = 450$  nm) and luminesces strongly in the red ( $\lambda_{max} \approx 620$  nm). Studies of the luminescence intensity as a function of air pressure indicate that the luminescence of the RudpCl/PDMS film is strongly quenched by atmospheric oxygen. Stern–Volmer plots of the luminescence intensity data over the 0–14 psi range can be obtained by plotting the ratio of the intensity at zero pressure to intensity at pressure,  $I_{em}^0/I_{em}$ , vs the pressure  $P$ . This results in a nearly linear relation ( $I_{em}^0/I_{em} = 1 + K_{SV}P$ ) and yields a Stern–Volmer quenching constant  $K_{SV}$  of 0.70 psi<sup>-1</sup>. This  $K_{SV}$  value is significantly less than previously reported by Xu et al.<sup>19</sup> for RudpCl in ostensibly the same PDMS material ( $K_{SV} \approx 4.9$  psi<sup>-1</sup>). However, the oxygen sensitivity of our RudpCl/PDMS system, as reflected by  $K_{SV}$ , is comparable to or greater than that of other PSP systems based on PDMS binders.<sup>1</sup>

The temperature dependence of the luminescence from RudpCl was investigated in two media (ethanol and PDMS) by monitoring the emission intensity and the emission decay lifetimes. The temperature dependence of the emission intensity quantitatively followed the same trends as observed for  $\tau$  (or  $\langle\tau\rangle$ ), but because more information concerning the luminescence decay dynamics is available from the lifetime studies, we focus on those data.

Table 1 contains the emission decay lifetimes of RudpCl in air-saturated and argon degassed ethanol over the temperature range

**Table 1** Emission intensity and decay lifetimes for RudpCl in ethanol<sup>a</sup>

$T, ^\circ\text{C}$	Air saturated $\tau$ , ns	Argon degassed $\tau$ , ns	Argon degassed $I_{\text{em}}$ , relative <sup>b</sup>
8		6210	6210
14	295		
18	283	5320	5170
23	273		
29		4390	4030
30	272		
34		4200	3510
36	277		
39	280		
42		3280	2680
43	285		

<sup>a</sup>Estimated error in lifetimes is  $\pm 5\%$ .<sup>b</sup>Relative emission intensity normalized to emission lifetime in argon degassed solution at 8  $^\circ\text{C}$ .**Table 2** Emission intensity and decay lifetimes for RudpCl in PDMS at 1-atm air pressure

Temp, $^\circ\text{C}$	$\alpha_1$	$\tau_1$ , ns	$\alpha_2$	$\tau_2$ , ns	$\alpha_3$	$\tau_3$ , ns	$\langle\tau\rangle$ , ns	$I_{\text{em}}$ , relative <sup>a</sup>
8	0.74	32	0.24	343	0.02	2450	158	158
15	0.75	28	0.22	307	0.02	2330	138	147
22	0.75	28	0.22	283	0.02	2290	134	137
32	0.77	27	0.21	254	0.02	2190	119	122
38	0.78	27	0.20	252	0.02	2190	116	113
43	0.77	24	0.21	225	0.02	1890	106	105
50	0.80	20	0.19	206	0.02	1870	84	95

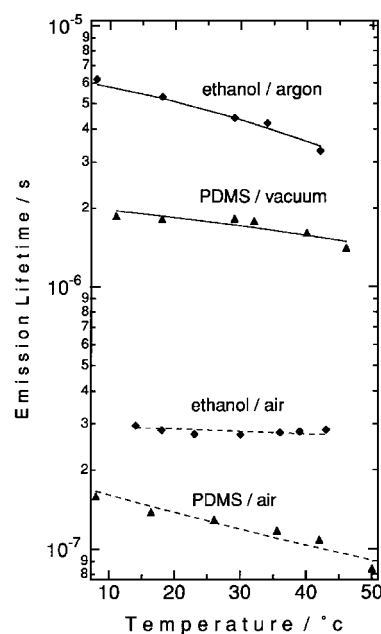
<sup>a</sup>Relative emission intensity normalized to median emission lifetime at 8  $^\circ\text{C}$ .**Table 3** Emission intensity and decay kinetics for RudpCl in PDMS under vacuum

Temp, $^\circ\text{C}$	$\alpha_1$	$\tau_1$ , ns	$\alpha_2$	$\tau_2$ , ns	$\alpha_3$	$\tau_3$ , ns	$\langle\tau\rangle$ , ns	$I_{\text{em}}$ , relative <sup>a</sup>
11	0.62	62	0.09	539	0.30	6010	1870	1870
18	0.61	60	0.10	678	0.29	5850	1810	1740
29	0.61	65	0.10	1340	0.29	5640	1820	1570
32	0.61	65	0.10	1540	0.29	5450	1780	1530
40	0.60	62	0.11	1390	0.29	4880	1600	1430
46	0.61	55	0.11	759	0.26	4550	1400	1370

<sup>a</sup>Relative emission intensity normalized to median emission lifetime at 11  $^\circ\text{C}$ .

from 10 to 40  $^\circ\text{C}$ . In every case the emission decays obeyed Eq. (5) for at least three lifetimes, indicating that, as expected, RudpCl decays according to a first-order kinetic model. The emission lifetimes are significantly shorter for the air-saturated solutions owing to the quenching by oxygen. Close inspection of the data reveals that the lifetime in the argon degassed solution decreases monotonically with increasing temperature; however, the emission lifetime is constant within experimental error for the air-saturated solution over the temperature range examined. Table 1 also contains a listing of the temperature dependence of the steady-state emission intensity of the RudpCl in ethanol, in arbitrary units normalized to correspond to the emission lifetimes. These data reveal that the total emission intensity decreases in parallel with the decrease in  $\tau$  for the argon degassed sample.

Tables 2 and 3 contain listings of the parameters obtained from fits of the emission decays of the air-saturated and vacuum degassed RudpCl/PDMS samples according to Eqs. (6) and (7). As noted in Sec. III, the emission decays of the RudpCl/PDMS films are nonexponential owing to the heterogeneous nature of the polymer matrix. In both air-saturated and vacuum degassed samples the emission decays are characterized by short, middle, and long emission lifetime components ( $\tau_1$ ,  $\tau_2$ , and  $\tau_3$ , respectively); the contribution of each component to the total decay is reflected by the corresponding amplitude factors  $\alpha_i$ . Oxygen has a pronounced effect on the overall emission decay of the RudpCl/PDMS film as reflected by the greater than tenfold lower  $\langle\tau\rangle$  in the presence of air compared

**Fig. 2** Plots of emission lifetime,  $\tau$  or  $\langle\tau\rangle$ , as a function of temperature: experimental data indicated by polygons; solid lines indicate fits to data in deoxygenated samples according to Eq. (8) (see text); dashed line indicate fits to data in air-saturated samples according to Eq. (9) (see text).

to under vacuum. The oxygen quenching has the most pronounced effect on the long lifetime component ( $\tau_3$ ) as indicated by the substantial decrease in both the lifetime and amplitude of this component. Temperature also has a pronounced effect on the emission decay kinetics for both the air-saturated and vacuum degassed samples. In each case,  $\langle\tau\rangle$  decreases with increasing temperature. For the vacuum degassed sample,  $\langle\tau\rangle$  decreases by approximately 25% over the 10–50  $^\circ\text{C}$  range, and for the air-saturated sample a 45% decrease in  $\langle\tau\rangle$  is seen over the same temperature range. Tables 2 and 3 also contain a listing of the temperature dependence of the steady-state emission intensity  $I_{\text{em}}$  of the RudpCl/PDMS film. In each case, the emission intensity is provided in relative units, which are normalized to correspond to the median emission lifetimes. Inspection of these data reveals that overall the decrease in  $I_{\text{em}}$  with increasing temperature generally parallels the decrease in  $\langle\tau\rangle$ .

Figure 2 illustrates a plot of  $\tau$  (or  $\langle\tau\rangle$ ) as a function of temperature for RudpCl in ethanol and in PDMS films in the presence of air and under vacuum (or argon). This figure reveals several qualitative trends that are pertinent with respect to understanding the origin of the temperature dependence of PSP formulations. First, the temperature dependence of  $\tau$  is qualitatively similar for RudpCl in ethanol/argon and in PDMS/vacuum. This similarity suggests that the intrinsic temperature dependence of the luminescence lifetime of the dye is not strongly influenced by the medium. By contrast, the temperature dependence of  $\tau$  for the PDMS/air sample is substantially greater than for the ethanol/air sample. Indeed, in the latter system  $\tau$  is virtually temperature independent. Finally, note that  $\tau$  is more strongly temperature dependent for PDMS/air than for PDMS/vacuum, despite the overall lifetime of the latter system being substantially larger. The observation of a comparatively strong temperature dependence for PDMS/air implies that in this case the temperature dependence is determined by the temperature dependence of the oxygen quenching pathway (i.e.,  $k_q[\text{O}_2]$ ).

## V. Analysis of Temperature Dependence Data

The temperature dependence of the luminescence decay of polypyridyl Ru(II) complexes has been the subject of numerous investigations.<sup>12–17</sup> Typically for samples in fluid, homogeneous solutions under vacuum, the temperature dependence of the lifetime is described by an equation of the form<sup>13–15</sup>

$$1/\tau = k_r + A_{\text{nr}} \exp\{-E_{\text{nr}}/RT\} \quad (8)$$

where  $k_r$  is the (temperature independent) radiative decay rate and  $A_{\text{nr}}$  and  $E_{\text{nr}}$  are, respectively, the frequency factor and activation

**Table 4** Arrhenius activation parameters from analysis of temperature dependence data

Environment	$k_r$ , s <sup>-1</sup>	$A_{nr}$ , s <sup>-1</sup>	$E_{nr}$ , kcal/mol	$A_q$ , s <sup>-1</sup>	$E_q$ , kcal/mol
Ethanol	$1.3 \times 10^5$	$1.9 \times 10^{10}$	7.3		
argon					
PDMS	$4.1 \times 10^5$	$8.0 \times 10^8$	5.1		
vacuum					
Ethanol	$1.3 \times 10^5$	$1.9 \times 10^{10}$	7.3	$4.6 \times 10^6$	<0.2
1-atm air					
PDMS	$4.1 \times 10^5$	$8.0 \times 10^8$	5.1	$6.7 \times 10^8$	2.7
1-atm air					

energy for the nonradiative decay channel. This equation implies that in the absence of oxygen, the temperature dependence of the emission lifetime (and  $I_{em}$ ) is due entirely to the temperature dependence of  $k_{nr}$ . Equation (8) is supported by quantum molecular theory, which indicates that  $k_r$  is only weakly temperature dependent (because of the temperature dependence of the refractive index of the medium).<sup>14</sup> By contrast, the nonradiative decay channel primarily involves transfer of thermal energy from the luminescent molecule to the surrounding medium (i.e., the solvent or polymer host) and the rate of this energy transfer process is temperature dependent.<sup>13,14</sup>

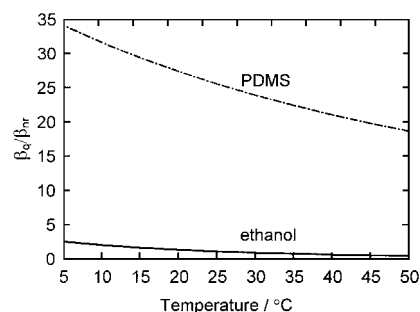
Now we turn to analysis of the temperature dependent luminescence data for the ethanol/argon and PDMS/vacuum systems. First, the temperature dependence of the ratio  $I_{em}/\tau$  (or  $I_{em}/\langle\tau\rangle$ ) is relatively constant over the temperature range studied. Because the intensity-lifetime ratio is proportional to  $k_r$  [Eq. (4)], this feature indicates that, as expected, the radiative decay rate for the RudpCl dye varies little with temperature in ethanol and PDMS. Next, the temperature dependent lifetime data for the ethanol and PDMS systems were fitted according to Eq. (8), and the parameters from the fits are listed in Table 4. Figure 2 compares the experimental data (points) with the lifetimes calculated by the fitting procedure (solid lines). The temperature dependent data for the samples in the absence of air are consistent with  $k_r \approx 10^5$  s<sup>-1</sup>,  $A_{nr} \approx 10^9$ – $10^{10}$  s<sup>-1</sup>, and  $E_{nr} \approx 5$ – $7$  kcal/mol. These parameters are very similar to those obtained from the temperature dependence of the luminescence in related polypyridine ruthenium dyes, which indicates there is nothing unusual about the RudpCl probe.<sup>13–15</sup> Also, it is significant that  $k_r$ ,  $A_{nr}$ , and  $E_{nr}$  for the dye in ethanol and PDMS are not substantially different. This is a clear indication that despite the complexity of the luminescence kinetics of the dye in PDMS (i.e., multiexponential decays), the overall temperature dependence of the emission from the dye is not strongly influenced by the PDMS matrix. This leads us to conclude that the temperature dependence, which is intrinsic to the dye, is not strongly affected by the polymer matrix.

Next we turn to analysis of the temperature dependent luminescence data for ethanol and PDMS samples at 1-atm air pressure. First, as already noted,  $k_{em}$  and  $\tau$  for the dye in ethanol or PDMS are significantly lower at 1-atm air pressure due to the oxygen quenching pathway (Fig. 1). The substantial diminution of  $\tau$  and  $I_{em}$  in air indicates that under this condition oxygen quenching is by far the major decay pathway. This fact alone allows the conclusion that at 1-atm pressure the temperature dependence must mainly be due to the temperature dependence of the oxygen quenching pathway. Indeed, it is possible to determine the relative importance of the oxygen quenching and the normal decay channels (i.e., radiative and nonradiative decay) at 1-atm pressure by applying Eqs. (2) and (3). Using  $\tau$  (or  $\langle\tau\rangle$ ) values at 29°C, we calculate that in ethanol ( $k_r + k_{nr} \approx 2 \times 10^5$  s<sup>-1</sup> and  $k_q[O_2] \approx 3.4 \times 10^6$  s<sup>-1</sup>, whereas in PDMS ( $k_r + k_{nr} \approx 5 \times 10^5$  s<sup>-1</sup> and  $k_q[O_2] \approx 7 \times 10^6$  s<sup>-1</sup>). In both cases, oxygen quenching is greater than tenfold faster than the natural decay rate; therefore, oxygen quenching accounts for >90% of the total decay of the luminescent RudpCl molecules.

Analysis of the experimental luminescence data at 1-atm pressure was carried out by fitting the temperature dependent emission lifetime data according to Eq. (9):

$$1/\tau = k_r + A_{nr} \exp\{-E_{nr}/RT\} + A_q \exp\{-E_q/RT\} \quad (9)$$

where  $A_q$  and  $E_q$  are, respectively, the frequency factor and activation energy for the oxygen quenching pathway. While fitting the


**Fig. 3** Plot of  $\beta_q/\beta_{nr}$  as a function of temperature.

experimental luminescence data at 1-atm pressure to Eq. (9),  $k_r$ ,  $A_{nr}$ , and  $E_{nr}$  were set equal to the values obtained by analysis of the data for the deoxygenated samples. Table 4 contains the parameters obtained from the fits of the 1-atm pressure data, whereas Fig. 2 compares the experimental data (points) with the lifetimes calculated by the fitting procedure (dashed lines). First, the analysis indicates that in ethanol the oxygen quenching pathway is characterized by a vanishingly small activation energy ( $E_q < 0.2$  kcal/mol) and a low-frequency factor ( $A_q \approx 5 \times 10^6$  s<sup>-1</sup>). By contrast, in PDMS oxygen quenching has  $E_q \approx 2.7$  kcal/mol and  $A_q \approx 7 \times 10^8$  s<sup>-1</sup>. The substantially larger  $E_q$  value for PDMS compared to ethanol is the origin of the much stronger temperature dependence observed in the former medium.

To further illustrate the importance of the oxygen quenching pathway to the temperature dependence of the RudpCl/PDMS system, we take the derivative of Eq. (9) with respect to temperature to give

$$\frac{\partial(1/\tau)}{\partial T} = \beta_{nr} + \beta_q \quad (10)$$

where

$$\beta_{nr} = \frac{A_{nr} E_{nr}}{RT^2} \exp\left\{-\frac{E_{nr}}{RT}\right\} \quad (11)$$

and

$$\beta_q = (A_q E_q / RT^2) \exp\{-E_q / RT\} \quad (12)$$

The intrinsic temperature dependence of the luminescent dye due to nonradiative decay is given by  $\beta_{nr}$ , and the temperature dependence resulting from the oxygen quenching pathways is given by  $\beta_q$ . The ratio  $\beta_q/\beta_{nr}$  is plotted in Fig. 3 for both the RudpCl/PDMS and the RudpCl/ethanol systems. Over the temperature range investigated, the ratio  $\beta_q/\beta_{nr}$  ranges from 18 to 34 for the PDMS system and from 0.4 to 2.5 for the ethanol system. Again, this difference is due to the much greater impact of the oxygen quenching pathway on the temperature dependence of the PDMS system. The oxygen quenching pathway is the dominant source of temperature dependence for the PDMS system. This result is in sharp contrast with the ethanol system, for which the oxygen quenching pathway and the nonradiative decay mechanism have roughly equivalent impact on the temperature dependencies.

The significance of the empirically determined  $E_q$  values for PDMS and ethanol can be appreciated by considering the factors that contribute to the temperature dependence of oxygen quenching. As noted, the observed rate of quenching by oxygen is given by the product  $k_q[O_2]$ . Both terms of this product could contribute to the overall temperature dependence: thus, the temperature dependence, as reflected by  $E_q$ , may be a composite of the temperature dependence of  $k_q$  and the oxygen concentration in the ethanol or PDMS.

The solubility of diatomic gases in condensed liquids or polymers is very weakly temperature dependent.<sup>20,21</sup> As a result, the oxygen concentration in ethanol or PDMS does not vary substantially over the temperature range examined. Therefore, this term can be ruled out as contributing significantly to the experimentally observed temperature dependence in the PDMS/air system.

The temperature dependence of  $k_q$  arises because the diffusivity of oxygen,  $D_{oxygen}$ , is temperature dependent. Stokes law indicates that  $D_{oxygen}$  in fluid solvents such as ethanol is proportional to absolute

temperature.<sup>21,22</sup> Only a narrow temperature range was investigated (283–323 K). Over this range  $D_{\text{oxygen}}$  does not vary substantially in ethanol, which explains the lack of a temperature dependence of the emission lifetime (and therefore  $k_q$ ) in this medium. By contrast,  $D_{\text{oxygen}}$  is expected to be more strongly temperature dependent in PDMS. This is because the diffusion of small molecules in polymers is a thermally activated process that involves cooperative motion of the polymer chains. As a result, the diffusivity varies with temperature according to an Arrhenius-type relationship (i.e.,  $D \propto \exp\{-E_a/RT\}$ ) (Refs. 20 and 21). Indeed, the activation energy determined for  $k_q$  in PDMS (2.7 kcal/mol) is in excellent agreement with the literature value for the activation energy for  $D_{\text{oxygen}}$  in the same polymer ( $E_a = 2.1$  kcal/mol) (Ref. 21). This excellent correspondence provides very good evidence that for the PDMS/air system, the temperature dependence is determined by the temperature dependence of  $D_{\text{oxygen}}$ .

Looking further at the pseudo-first-order quenching rate  $k_q[\text{O}_2]$  and considering the earlier arguments, the oxygen concentration in the polymer may be modeled by Henry's law (i.e.,  $[\text{O}_2] = SP$ ), with the solubility  $S$  being temperature independent. The  $k_q$  term is proportional to the diffusivity and is modeled by an Arrhenius-type expression (i.e.,  $k_q \propto D = D_0 \exp\{-E_a/RT\}$ ). Our model for  $k_q[\text{O}_2]$  comes from the last term in Eq. (9) as  $k_q[\text{O}_2] = A_q \exp(-E_q/RT)$ . The preexponential term  $A_q$  is seen to be linearly related to the preexponential constant for the diffusivity  $D_0$ , the solubility  $S$ , and the static pressure at the free surface  $P$ . This shows that the pressure dependence of the PSP coating is contained in the preexponential term  $A_q = A_q(P)$ . Although the present studies were not extended to include intermediate air pressures between 0 and 1 atm, it is possible to use the parameters listed in Table 4 to linearly interpolate the temperature model of the RudPCI/PDMS paint [Eq. (9)] to intermediate air pressures using the expression

$$A_q(P) = (P/P_{\text{atm}}) A_q^{1\text{atm}} \quad (13)$$

where  $P$  is air pressure above the PSP coating and  $A_q^{1\text{atm}}$  is the  $A_q$  value listed in Table 4 at  $P = 1$  atm.

## VI. Summary and Conclusion

A study is reported of the temperature dependence of the luminescence decay lifetime for a typical pressure sensitive paint formulation consisting of a luminescent polypyridine ruthenium(II) dye dispersed in a polydimethylsiloxane binder. The results indicate that the temperature dependence in the absence of air is dominated by the intrinsic temperature dependence of the nonradiative decay rate of the luminescent probe molecule. However, at 1-atm air pressure, the temperature dependence of the luminescence lifetime and intensity of the paint is determined by the temperature dependence of the diffusivity of oxygen in the polymer matrix. This study clearly indicates that to minimize the temperature dependence of the paint formulation it is necessary to design the binder system to have the lowest possible activation energy for oxygen diffusivity. Although the temperature dependence studies were not extended to include air pressures between 0 and 1 atm, the parameters obtained by analysis of the temperature dependence data at 0- and 1-atm air pressures allow interpolation to intermediate pressures. This interpolation may prove useful in predicting the temperature dependence of pressure sensitive paint formulations in real-world applications.

## References

- Morris, M. J., Donovan, J. F., Kegelman, J. T., Schwab, S. D., Levy, R. L., and Crites, R. C., "Aerodynamic Applications of Pressure Sensitive Paint," *AIAA Journal*, Vol. 31, No. 3, 1993, pp. 419–425.

- McLachlan, B. G., Bell, J. H., Park, H., Kennelly, R. A., Schreiner, J. A., Smith, S. C., Strong, J. M., Gallery, J., and Gouterman, M., "Pressure-Sensitive Paint Measurements on a Supersonic High-Sweep Oblique Wing Model," *Journal of Aircraft*, Vol. 32, No. 2, 1995, pp. 217–227.
- Morris, M. J., "Use of Pressure-Sensitive Paints in Low-Speed Flows," *ICIASF 95 Record, International Congress on Instrumentation in Aerospace Simulation Facilities* (Wright-Patterson AFB, OH), Inst. of Electrical and Electronics Engineers, New York, 1995, pp. 31.1–31.10 (IEEE Publication 95CH3482-7).
- Burns, S. P., and Sullivan, J. P., "The Use of Pressure Sensitive Paints on Rotating Machinery," *ICIASF 95 Record, International Congress on Instrumentation in Aerospace Simulation Facilities* (Wright-Patterson AFB, OH), Inst. of Electrical and Electronics Engineers, New York, 1995, pp. 32.1–32.14 (IEEE Publication 95CH3482-7).
- Bell, J. H., and McLachlan, B. G., "Image Registration for Luminescent Paint Sensors," *AIAA Paper 93-0178*, Jan. 1993.
- Donovan, J. F., Morris, M. J., Pal, A., Benne, M. E., and Crites, R. C., "Data Analysis Techniques for Pressure- and Temperature-Sensitive Paints," *AIAA Paper 93-0176*, Jan. 1993.
- Carroll, B. F., Abbitt, J. D., Lukas, E. W., and Morris, M. J., "Step Response of Pressure Sensitive Paints," *AIAA Journal*, Vol. 34, No. 3, 1996, pp. 521–526.
- Sajben, M., "Uncertainty Estimates for Pressure Sensitive Paint Measurements," *AIAA Journal*, Vol. 31, No. 11, 1993, pp. 2105–2110.
- Oglesby, D. M., "Wind Tunnel Barometry by Means of Fluorescence and Phosphorescence Quenching," *Inter-American Photochemical Society Newsletter*, Vol. 18, No. 2, 1995, pp. 20–32.
- Bacon, J. R., and Demas, J. N., "Determination of Oxygen Concentrations by Luminescence Quenching of a Polymer-Immobilized Transition-Metal Complex," *Analytical Chemistry*, Vol. 59, No. 23, 1987, pp. 2780–2785.
- Boens, N., DeRoeck, T., Dockx, J., and DeSchryver, F. C., *DECAN*, version 1.0, Katholieke Universiteit Leuven, Belgium, Dec. 1991.
- Watts, R., "Ruthenium Polypyridyls. A Case Study," *Journal of Chemical Education*, Vol. 63, No. 10, 1983, pp. 834–842.
- Van Houten, J., and Watts, R., "Temperature Dependence of the Photophysical and Photochemical Properties of the Tris(2,2'-dipyridyl) ruthenium(II) Ion in Aqueous Solution," *Journal of the American Chemical Society*, Vol. 98, No. 16, 1976, pp. 4853–4858.
- Caspar, J. V., "Excited State Decay Processes in Osmium(II), Ruthenium(II) and Rhenium(I) Polypyridyl Complexes," Ph.D. Dissertation, Dept. of Chemistry, Univ. of North Carolina, Chapel Hill, NC, 1982.
- Wacholtz, W. F., Auerbach, R. A., and Schmehl, R. H., "Independent Control of Charge-Transfer and Metal-Centered Excited States in Mixed-Ligand Polypyridine Ruthenium(II) Complexes via Specific Ligand Design," *Inorganic Chemistry*, Vol. 25, No. 2, 1986, pp. 227–234.
- Sacksteder, L.-A., Lee, M., Demas, J. N., and DeGraff, B. A., "Long-Lived, Highly Luminescent Rhenium(I) Complexes as Molecular Probes: Intra- and Intermolecular Excited State Interactions," *Journal of the American Chemical Society*, Vol. 115, No. 18, 1993, pp. 8230–8238.
- Juris, A., Balzani, V., Barigelli, F., Campagna, S., Belser, P., and von Zelewski, A., "Ru(II) Polypyridine Complexes: Photophysics, Photochemistry, Electrochemistry and Chemiluminescence," *Coordination of Chemistry Reviews*, Vol. 84, No. 1, 1988, pp. 85–277.
- James, D. R., Liu, Y.-S., DeMayo, P., and Ware, W. R., "Distributions of Fluorescence Lifetimes: Consequences for the Photophysics of Molecules Adsorbed on Surfaces," *Chemical Physics Letters*, Vol. 120, No. 4/5, 1985, pp. 460–465.
- Xu, W., McDonough, R. C., III, Langsdorf, B., Demas, J. N., and DeGraff, B. A., "Oxygen Sensors Based on Luminescence Quenching: Interactions of Metal Complexes with the Polymer Supports," *Analytical Chemistry*, Vol. 66, No. 23, 1994, pp. 4133–4141.
- Naylor, T., "Permeation Properties," *Comprehensive Polymer Science*, Vol. 2, edited by G. Allen and J. C. Bevington, Pergamon, Oxford, England, UK, 1989, pp. 643–668.
- Pauly, S., "Permeability and Diffusion Data," *Polymer Handbook*, 3rd ed., edited by J. Brandrup and E. H. Immergut, Wiley-Interscience, New York, 1989, pp. VI/435–VI/449.
- Laidler, K. J., *Chemical Kinetics*, 3rd ed., Harper and Row, New York, 1987, p. 214.