

different temperatures. The Bjerrum treatment itself allows  $a$  to be calculated from the  $Q(b)$  function.  $K$  is the same for any value of  $c$  for a particular temperature and is given, for dilute solutions, by the equation

$$\frac{1}{K} = \frac{4\pi N}{1000} \left( \frac{|z_1 z_2| e^2}{D k T} \right)^3 Q(b)$$

where  $Q(b) = \int_2^b x^{-4} e^{-x} dx$  and  $b = \frac{|z_1 z_2| e^2}{D k T a}$

In table IV the values of  $a$  are recorded, for each temperature; in the third column of the table are the critical Bjerrum distances. Both the distance of the closest

Table IV

VALUES OF THE CLOSEST APPROACH AND THE BJERRUM CRITICAL DISTANCE AT VARIOUS TEMPERATURES

Temperature	$a$	$q$
25°C	7.1	8.1
45	6.2	8.4
55	3.6	8.7
75	2.6	9.4

approach and the Bjerrum critical distance show systematic variations, though in opposite senses. In the critical distance, the variations is clearly acceptable because the product  $DT$  is not constant and the critical distance, given by

$$q = \frac{|z_1 z_2| e^2}{2 D k T},$$

must therefore also vary. It is more difficult to accept the change on the parameter  $a$  which is implied to be a constant by the Fuoss theory.

The use of the Fuoss and Bjerrum theories of association leads to unsatisfactory values for the parameter  $a$

which in turn invalidates the simple assumption that the Onsager equation needs only be corrected for the effect of ion association.

Since the ionic association constants,  $K_A$ , are small, it is possible to analyse the experimental data using the solution of the Fuoss-Onsager equation (10) for associated electrolytes

$$\Lambda = \Lambda^0 - S(c\gamma)^{\frac{1}{2}} + Ec\gamma \log c\gamma + Jc\gamma - K_A \Lambda^0 f^2 c\gamma$$

The computation was performed on a 650 IBM computer using an adaptation of Kay's Fortran program (1). The results obtained are given in table V.

It can readily be seen that the  $\Lambda^0$  values are not significantly different from those previously computed in the sense that the agreement is within the precision of the experimental results and that the differences are not systematic.

All the computed values of  $K_A$  probably lack physical meaning.

The distances of closest approach are all of reasonable magnitude.

Since our attention is mainly directed to the  $\Lambda^0$  values and their temperature and pressure dependence, we

Table V

PARAMETERS OF THE FUOSS-ONSAGER EQUATION FOR ASSOCIATED ELECTROLYTES

$t$	$\Lambda^0$	$K_A$	$a$	$E$	$J$	$\partial J / \partial a$
25°C	32.46	0.161	2.6	63.83	291.1	96.26
45	44.86	4.92	2.7	103.7	475.9	146.1
55	51.56	— 1.96	2.1	131.5	484.6	204.4
75	65.61	— 11.0	1.9	213.8	697.4	337.8

(1) We are indebted to Dr. R. L. Kay of the Mellon Institute, Pittsburg, Pa. that kindly provided the Fortran program, to the director of the Centro de Cálculo Científico — Fundação Calouste Gulbenkian —, who kindly allowed the use of the computer, and to Mr. A. Cadete, of the same Centro, for the adaptation of the program.

decided to perform a preliminary test of their consistency using the various sets of results, i. e. by evaluating the mean enthalpy of activation at constant pressure over the studied temperature range from the relation

$$\Delta H_o^* = RT^2 \left( \frac{\partial \ln \Lambda^o}{\partial T} \right)_P$$

The resultant mean enthalpies of activation are respectively 2907, 2906 and 2906 cal mole<sup>-1</sup> from the  $\Lambda^o$  values recorded in tables II, III and V. There is no significant difference, and it is evident that for the purposes of investigating the nature of  $\Lambda_o$ , all three extrapolation procedures are equally satisfactory. This is an important conclusion for the study of those systems for which the solvent parameters required to utilise the extended theories are not available.

#### ACKNOWLEDGMENT

The authors wish to thank Prof. G. J. HILLS, of the Southampton University, for helpful discussions.

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#### RESUMO

Mediu-se a condutibilidade de soluções de picrato de tetra-etilamónio em nitrobenzeno anidro a várias concentrações e temperaturas. Examinaram-se as possibilidades de utilização de diferentes fórmulas de extrapolação, recorrendo a dados da literatura para a variação da viscosidade e da constante dielétrica do nitrobenzeno com a temperatura.

Há pequenas discrepâncias entre os valores da condutibilidade equivalente limite obtida pelas diferentes extrapolações, mas todos eles conduzem a valores idênticos para a entalpia de activação para a condutibilidade.



# NONRADIATIVE ENERGY TRANSFER FROM BENZENE TO 2,5-DIPHENYLOXAZOLE AND 2,2'-p-PHENYLENE-bis-(5-PHENYLOXAZOLE)

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*Stern-Volmer constants for the nonradiative energy transfer from benzene to 2,5-diphenyloxazole (PPO) and 2,2'-p-phenylene-bis-(5-phenyloxazole) (POPOP) when benzene is excited by u. v. radiation are determined for both deoxygenated and air-equilibrated solutions. It is found that the transfer efficiency is greater with POPOP solutions and the significance of this fact is discussed. The half value concentrations for monomer-excimer equilibrium of PPO solutions in benzene are also given.*

## 1 — INTRODUCTION

In a binary system where the energy donor (the solvent) is liquid at room temperature (e. g. benzene) the rate parameters for nonradiative energy transfer to an energy acceptor (the solute) are greater than those based on FÖRSTER'S (1) theory of resonance transfer (2) (3) (4). Material diffusion and/or energy migration between solvent molecules have been considered in several theoretical (5) (6) (7) and experimental works (8) (9) (10) as contributing to the overall energy transfer process, according to an early suggestion by KALLMANN and FURST (11).

Only recently (12) (13) the fact that the solvent molecules may form excimers due to an interaction between an excited and a ground state molecule has been taken into account in the evaluation of energy transfer rates.

It has been suggested (14) that energy migration might be due to excimer formation and dissociation, which would lead, for large solvent concentrations, to an efficient diffusion-migration controlled energy transfer by collision.

In a recent work, LUDWIG & AMATA (15) have proposed that different excimer and monomer quenching constants could account for the variation of the overall quenching effect of  $\text{CCl}_4$  with solvent dilution, energy migration in the solvent being unimportant. Similar results were interpreted, however, as showing the effect of energy migration without invoking an excimer mechanism (16) (17).

It is thus clear that although excimers must be involved in the energy process when the energy donor is an excimer forming molecule the actual role of the excimer in the process is not fully understood.

The present work reports measurements on the fluorescence emission from binary solutions of 2,5 diphenyloxazole (PPO) and 2,2'-p-phenylene-bis-(5-phenyloxazole) (POPOP) in benzene. The first of these systems was chosen in order to verify previously reported (14) energy transfer coefficients obtained through excitation spectra measurements. On the other hand, the study of the properties of POPOP as an energy acceptor from benzene was considered of interest for a detailed study of the ternary system Benzene-PPO-POPOP (18), since POPOP has already been reported to be an efficient energy acceptor from PPO which justifies its use as a «wavelength shifter» with PPO solutions (19).

## 2 — THEORY

Let us consider a binary system containing a solvent X (molar concentration  $c_X$ ) and a solute Y (molar concentration  $c_Y$ ) excited by u. v. radiation (intensity  $I_0$  einstein  $s^{-1}$ ). If both solvent and solute form excimers and solvent-solute energy transfer can occur both from the excimer and excited monomer solvent molecules to the solute monomer, the intensities of monomer and excimer solute emission are given, respectively, by (20)

$$I_{MY} = I_0 q_{MY} \frac{c_{hY}}{c_Y + c_{hY}}$$

$$I_{DY} = I_0 q_{DY} \frac{c_Y}{c_Y + c_{hY}}$$

if only the solute is excited. If the solvent is excited, direct solute excitation being usually small, and transfers its energy to the solute, the intensities of solute emission are given by

$$I_{XMY} = I_0 q_{MY} \frac{c_{hY}}{c_Y + c_{hY}} F_{YX}$$

$$I_{XDY} = I_0 q_{DY} \frac{c_Y}{c_Y + c_{hY}} F_{YX}$$

In these equations,  $q_{MY}$  and  $q_{DY}$  represent the solute monomer and excimer quantum efficiencies, respectively,  $c_{hY}$  the «half-value concentration» (21) and  $F_{YX}$  (denoted by  $F_{XY}$  in reference 20) the solvent-solute energy transfer coefficient. The energy transfer coefficient may be written in the form

$$F_{YX} = \frac{A_{YX} c_Y}{1 + A_{YX} c_Y}$$

The Stern-Volmer constant  $A_{YX}$  (denoted by  $A_Y$  in reference 20) is independent of solute concentration if the solvent monomer-excimer equilibrium is very fast compared with any process of monomer and excimer de-activation. The above equation can be used when the solute does not form excimers, making

$$\frac{c_{hY}}{c_Y + c_{hY}} \simeq 1$$

$$\frac{c_Y}{c_Y + c_{hY}} \simeq 0$$

Similar equations can be obtained when the solutions contain oxygen, the values of the rate constants being different and dependent on oxygen concentration (22).

## 3 — EXPERIMENTAL

The experimental arrangement has been described previously (20). Light from a mercury arc source (HP-100) monochromatised with a high intensity Bausch and Lomb monochromator was used for excitation. The fluorescence emission from the binary solutions was analysed with a 500 mm Bausch and Lomb grating monochromator. The current delivered by an E. M. I. 6256 B quartz window photomultiplier was measured with a galvanometer. All the measurements were made in reflection.

The 2537 Å mercury line was used to excite benzene. Direct excitation of PPO was achieved with the 3130 Å mercury line. As shown later, to study benzene-POPOP transfer there is no need to excite POPOP directly.

The solutions were deoxygenated by nitrogen bubbling and all the spectral intensities were normalized to the same intensity of excitation using a standard solution of POPOP.

Benzene (Merck, p. a.) was used as an energy donor, PPO (Fluka-puriss.) and POPOP (Fluka-puriss.) were used as acceptors.

## 4 — RESULTS AND DISCUSSION

Measurements were made of the fluorescence emission from solutions of PPO in benzene (XY system) and POPOP in benzene (XZ system). The relative intensities of solute emission were analysed in terms of the relationships indicated above.

For deoxygenated solutions, the intensities of PPO monomer emission (uncorrected for the spectral response of the monochromator-detector system) should obey the equation

$$i_{MY}(\lambda) = I_0 S_{MY}(\lambda) q_{MY} \frac{c_{hY}}{c_Y + c_{hY}}$$

if PPO is excited directly, and

$$i_{XMY}(\lambda) = I_0 S_{MY}(\lambda) q_{MY} \frac{c_{hY}}{c_Y + c_{hY}} \frac{A_{YX} c_Y}{1 + A_{YX} c_Y}$$

if there is transfer from benzene. In these equations,  $S_{MY}(\lambda)$ , which is wavelength dependent, is proportional to the calibration factor of the detector system (20). Thus,

$$\frac{c_Y}{r_{MY}(\lambda)} = \frac{1}{K_1(\lambda)} \left[ c_Y + \frac{1}{A_{YX}} \right]$$

where

$$r_{MY}(\lambda) = \frac{i_{XMY}(\lambda)}{i_{MY}(\lambda)}$$

and

$$\frac{1}{i_{MY}(\lambda)} = \frac{1}{K_2(\lambda)} \left[ 1 + \frac{c_Y}{c_{hY}} \right]$$

Linear relationships similar to those above can be obtained for the relative intensities from air-equilibrated solutions, yielding the values of a Stern-Volmer constant  $A'_{YX}$  and a half-value concentration  $c'_{hY}$ .

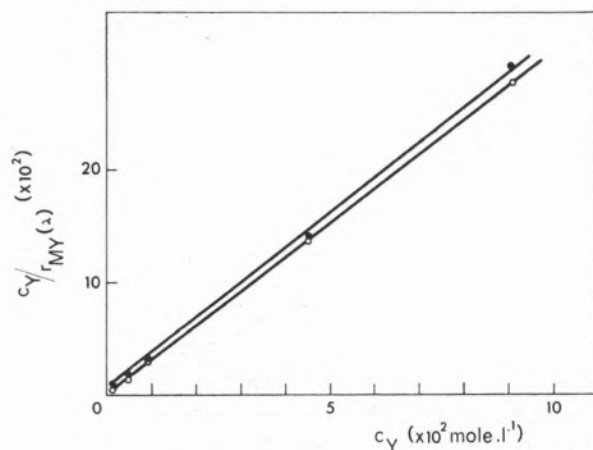


Fig. 1 — Variation of  $c_Y / r_{MY}(\lambda)$  with PPO concentration  $c_Y$ ;  $\lambda \approx 365 \text{ m}\mu$  (monomer emission);  $\circ$  — deoxygenated solutions;  $\triangle$  — air-equilibrated solutions.

Since POPOP does not show excimer emission, the equations above can be simplified. If  $c_Z$  denotes POPOP concentration, the relative intensities of POPOP emission (uncorrected for the spectral response) when

benzene molecules are excited and transfer their energy to POPOP should be given by

$$i_{XZ}(\lambda) = I_0 S_Z(\lambda) q_Z \frac{A_{ZX} c_Z}{1 + A_{ZX} c_Z}$$

Then

$$\frac{1}{i_{XZ}(\lambda)} = \frac{1}{K_3(\lambda)} \left[ c_Z + \frac{1}{A_{ZX}} \right]$$

From the variation of  $1/i_{XZ}(\lambda)$  with  $c_Z$  it is possible to obtain the Stern-Volmer constant  $A_{ZX}$ . Similarly, from measurements with air-equilibrated solutions it is possible to obtain a Stern-Volmer constant  $A'_{ZX}$ .

Figs. 1 and 2 show the variation of  $c_Y / r_{MY}(\lambda)$  and  $1/i_{MY}(\lambda)$  with PPO concentration  $c_Y$  — for both air-equilibrated and deoxygenated solutions. Fig. 3 shows the variation of  $1/i_{XZ}(\lambda)$  with POPOP concentration  $c_Z$ . In all cases the predicted linear variations are well verified.

From the straight lines in fig. 2 it is possible to obtain the half-value concentration  $c_{hY} = 0.37 \text{ mole.l}^{-1}$

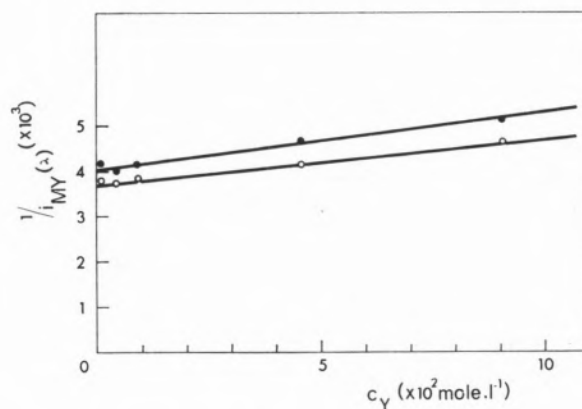


Fig. 2 — Variation of  $1/i_{MY}(\lambda)$  with PPO concentration  $c_Y$ ;  $\lambda \approx 365 \text{ m}\mu$  (monomer emission);  $\circ$  — deoxygenated solutions;  $\triangle$  — air-equilibrated solutions.

(deoxygenated solutions) and  $c'_{hY} = 0.31 \text{ mole.l}^{-1}$  (air equilibrated solutions) for PPO solutions in benzene. These values are to be compared with the value  $c_{hY} = 0.30 \text{ mole.l}^{-1}$  obtained by LAMI (23) for PPO solutions in cyclohexane.

From the straight lines in figs. 1 and 3 it is possible to obtain the Stern-Volmer constants for energy transfer



from benzene. The ratio between the slope and intercept yields  $A_{YX} = 1080 \text{ mole}^{-1} \cdot \text{l}$  (deoxygenated PPO solutions),  $A'_{YX} = 400 \text{ mole}^{-1} \cdot \text{l}$  (air equilibrated PPO solutions),  $A_{ZX} = 1385 \text{ mole}^{-1} \cdot \text{l}$  (deoxygenated POPOP solutions),  $A_{ZX} = 474 \text{ mole}^{-1} \cdot \text{l}$  (air equilibrated POPOP solutions).

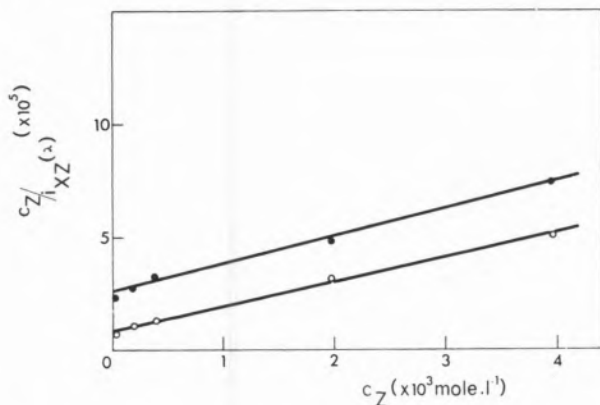


Fig. 3 — Variation of  $c_Z / i_{XZ}(\lambda)$  with POPOP concentration  $c_Z$ ;  $\lambda \simeq 450 \text{ m}\mu$ ;  $\circ$  — deoxygenated solutions;  $\triangle$  — air-equilibrated solutions.

Previously reported (14) values are  $A_{YX} = 1053 \text{ mole}^{-1} \cdot \text{l}$  and  $A'_{YX} = 364 \text{ mole}^{-1} \cdot \text{l}$  obtained from excitation spectra measurements.

On the other hand, a useful parameter is the quantity  $a = (A/A' - 1)$  which depends only on solvent rate constants (22). From the results above one obtains  $a_{YX} = 1.70$ ,  $a_{ZX} = 1.92$ , which can be compared with the reported (14) value of 1.89.

Figure 4 shows the emission spectra of benzene, PPO and POPOP and the absorption spectra of PPO and POPOP. FORSTER'S critical distances  $R_0$  for nonradiative energy transfer between the solvent and the solute are readily evaluated from

$$R_0^6 = \frac{9000 (\ln 10) \kappa^2 q_0}{128 \pi^5 \eta^4 N} \int_0^\infty \frac{I(\bar{\nu}) \epsilon(\bar{\nu})}{\bar{\nu}^4} d\bar{\nu}$$

where  $\kappa$  is an orientation factor, related with the transition dipole moments ( $\kappa^2 = 2/3$  for a random distribution)  $q_0$  is the quantum efficiency of the sensitizer fluorescence in the absence of acceptor,  $\eta$  is the refractive index,  $N$  is Avogadro's number,  $I(\bar{\nu})$  is the normalized relative sensitizer emission intensity and  $\epsilon(\bar{\nu})$  the molar extinction coefficient of the acceptor.

Substituting the values of the constants one obtains

$$R_0^6 = 5.87 \times 10^{-25} \frac{q_0}{\eta^4} \int_0^\infty \frac{I(\bar{\nu}) \epsilon(\bar{\nu})}{\bar{\nu}^4} d\bar{\nu}$$

Since for pure liquid benzene there is both monomer and excimer emission and since both monomer and excimer can probably transfer their energy to the solute, this fact must be taken into account when the  $R_0$  values are calculated. When both monomer and excimer solvent molecules have the same decay constants in the absence of the acceptor [which is the case for benzene (24)] the best way is to consider the overlap integral between the full emission spectrum of the solvent and the absorption spectrum of the solute, and an «average value» for the quantum efficiency calculated from monomer and excimer quantum efficiencies (22)

$$q_0 = \frac{q_M c_X + q_D c_{hX}}{c_X + c_{hX}}$$

where  $c_X$  is the solvent concentration ( $c_X = 11.2 \text{ mole} \cdot \text{l}^{-1}$  for pure liquid benzene),  $c_{hX}$  is the half-value concentration for solvent monomer-excimer emission and  $q_M$  and  $q_D$  are the solvent monomer and excimer

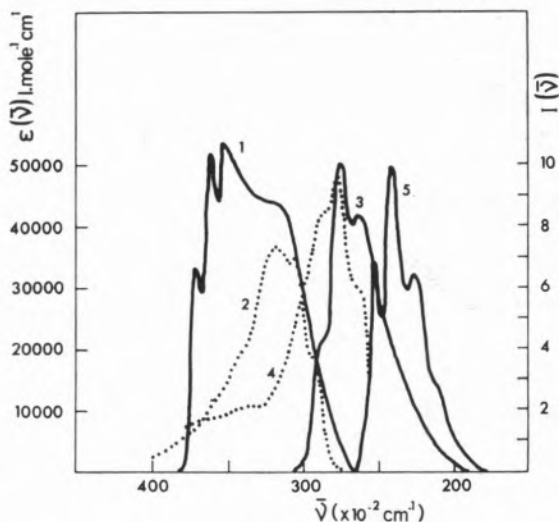


Fig. 4 — Absorption (dotted line) and emission (full line) spectra: (1) benzene emission; (2) PPO absorption; (3) PPO emission; (4) POPOP absorption; (5) POPOP emission. Curve (1) is taken from reference (24); curves (2) to (5) are from reference (25).

quantum efficiencies, respectively. Using the values (28)  $q_M = 0.05$ ;  $q_D = 0.012$ ,  $c_{hX} = 2.1 \text{ mole} \cdot \text{l}^{-1}$  one obtain  $q_o = 0.044$ . Since  $n = 1.4$ , the critical distances can be evaluated as  $R_{oYX} = 22.6 \text{ \AA}$  for PPO and  $R_{oZX} = 21.7 \text{ \AA}$  for POPOP.

The values of the critical distances can be used to evaluate the «theoretical» values of the Stern-Volmer constants, from the expression (27) (29) (22)

$$A_o = \frac{R_o^3}{1.935 \times 10^{-22}}$$

where  $R_o$  is expressed in cm and  $A_o$  in  $\text{mole}^{-1} \cdot \text{l}$ . Using the values  $R_{oYX}$  and  $R_{oZX}$  one obtains  $A_{oYX} = 59.8 \text{ mole}^{-1} \cdot \text{l}$ ,  $A_{oZX} = 52.6 \text{ mole}^{-1} \cdot \text{l}$  which are to be compared with the values  $A_{YX} = 1080 \text{ mole}^{-1} \cdot \text{l}$  and  $A_{ZX} = 1385 \text{ mole}^{-1} \cdot \text{l}$  obtained experimentally.

It is seen that not only the calculated values of the Stern-Volmer constants are much smaller than those obtained from the experimental results but also that the calculated  $A_{oYX}$  (for PPO) is greater than  $A_{oZX}$  (for POPOP) while the experimental value  $A_{YX}$  (for PPO) is smaller than  $A_{ZX}$  (for POPOP).

The fact that the Stern-Volmer constants obtained experimentally are much greater than those calculated has been observed in many cases (2) (4) (30) and usually interpreted as meaning that migration and/or material diffusion contribute to the overall energy transfer process. For some binary systems where the concentration of the energy donor was small, WARE (3) found a good correlation between the experimental and theoretical values of the Stern-Volmer constants. NORTHROP and SIMPSON (31), however, for some solid systems did not observe any correlation between transfer and overlap integrals.

Since Forster's theory is only valid when the molecules are stationary during the transfer process several attempts have been made to describe the overall energy transfer process including long range transfer, material diffusion and energy migration. This has been achieved either by introducing modifications into Forster's equations (32) or solving the diffusion equation with appropriate terms describing the long range transfer (33) (34) (35). Other theoretical approaches have been published, mainly applied to quenching processes (36) (37) (38) but including as possible cases resonance transfer. However, in all these cases the fact that the solvent does form excimers has not been taken into account.

The fact that the solvent excimer molecules as well as excited monomer can transfer their energy to the solute (12) shows that variations in the transfer efficiency with solute concentration can be due, at least partially, to the fact that the transfer rate constants from monomer and excimer may be different. In recently published work it has been considered either that energy migration does not exist (15) or that it is the same for both monomer and excimer or that it is only to be considered among solvent excited monomers (39).

An alternative explanation has been proposed (14) by which, for high solvent concentrations, energy migration among solvent molecules, which is considered to be due to successive excimer formations and dissociations, competes efficiently with the long range solvent-solute transfer. As a result, and at a first approximation, the energy transfer process becomes a diffusion-migration controlled collisional process. According to this mechanism, the rate constant for energy transfer is

$$k_{YX} = \frac{4 \pi N}{1000} (D_X + D_Y + \Lambda) R$$

where  $N$  is Avogadro's number,  $D_X$  and  $D_Y$  are the diffusion coefficients of solvent and solute molecules, respectively,  $\Lambda$  is the migration coefficient and  $R$  the interaction distance. For the B-POPOP and B-PPO systems the ratio between transfer constants will be then

$$\frac{k_{ZX}}{k_{YX}} = \frac{(D_X + D_Z + \Lambda) R_{ZX}}{(D_X + D_Y + \Lambda) R_{YX}}$$

Assuming  $R_{YX} = 6 \text{ \AA}$ ,  $D_X + D_Y = 4 \times 10^{-5} \text{ cm}^2 \text{ seg}^{-1}$ , it has been obtained (14)  $\Lambda = 6.8 \times 10^{-5} \text{ cm}^2 \text{ seg}^{-1}$ . If we assume now that  $R_{YX}$  equals the sum of a benzene radius ( $R_X \approx 1.5 \text{ \AA}$ ) and a radius for the PPO molecule ( $R_Y \approx 4.5 \text{ \AA}$ ) and that  $R_Z \approx 7.5 \text{ \AA}$  is the radius of the POPOP molecule we obtain  $R_{ZX} \approx 9 \text{ \AA}$ . Furthermore, the diffusion coefficients being proportional to the reciprocal of the molecular radius we may take  $D_Y \approx 10^{-5} \text{ cm}^2 \text{ seg}^{-1}$ ,  $D_X \approx 3 \times 10^{-5} \text{ cm}^2 \text{ seg}^{-1}$ ,  $D_Z \approx 0.6 \times 10^{-5} \text{ cm}^2 \text{ seg}^{-1}$ . Then  $k_{ZX}/k_{YX} \approx 1.45$ . The solvent being the same in the case of B-PPO and B-POPOP systems, the ratio between the Stern-Volmer energy transfer constants is just the ratio the energy transfer rate parameters, provided the monomer-excimer equilibrium in the solvent is fast compared with the rate

of transfer (12) which is the case for benzene. Then, from the experimental values  $A_{YX}$  and  $A_{ZX}$  we obtain  $k_{ZX}/k_{YX} \approx 1.28$  which compares well with the value above, if we consider the approximations involved in the derivation of the expression for  $k_{YX}$  and  $k_{ZX}$  and the fact that  $R_Z$  is certainly over estimated.

## ACKNOWLEDGEMENTS

The authors would like to thank Mr. D. V. LOURO, who helped with the measurements. A grant from NATO (Research Grant n.º 242) for the purchase of equipment is gratefully acknowledged.

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## RESUMO

Determinam-se as constantes de Stern-Volmer para o processo de transferência de energia não radiativa entre o benzeno e 2,5-difeniloxazole (PPO) e entre o benzeno e 2,2'-para-fenileno-bis (5-feniloxazole) (POPOP), quer em soluções contendo oxigénio quer em soluções sem oxigénio. Os resultados mostram ser maior a eficiência de transferência para as soluções de POPOP. Discute-se a importância deste facto. Determinam-se os valores das concentrações de semiextinção para soluções de PPO em benzeno.