

## EXCIPLEX-AROMATIC COMPLEX FORMATION

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### Summary

Red shifts and intensification of the emissions from pyrene-dimethylaniline and anthracene-dimethylaniline exciplexes on going from n-heptane to non-polar benzenoid solvents, such as benzene, *p*-xylol and mesitylene, have been attributed to formation of a complex between the exciplex and the aromatic during the lifetime of the exciplex. From a kinetic scheme for the fluorescence transformation the equilibrium constants for the complex formation have been estimated graphically for various systems.

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It is well known that, unlike the fluorescence of excimers, that of exciplexes exhibits an appreciable solvent dependence. The spectrum shifts towards the red with increasing dielectric constant of the solvent [1 - 5]. This has been attributed to the stabilization of the exciplex dipole by the orientation reaction field of the solvent dipole. Using this model the exciplex dipole moment has been calculated from the slope of the

$$\Delta\nu \text{ vs. } \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \text{ or } \frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2}$$

plot [4, 5], where  $\Delta\nu$  refers to a frequency shift in a solvent having a dielectric constant  $\epsilon$  and a refractive index  $n$  with respect to that in n-heptane. It has further been observed that the fluorescence intensity is considerably quenched in solvents of high dielectric constants, and that the quenching effect follows the Stern-Volmer mechanism.

According to this model it is expected that in all solvents having  $\epsilon = n^2$  the exciplex emission should appear at the same position. In the case of the exciplex emission from aromatic hydrocarbon-dimethylaniline systems this was found not to be the case. Figures 1 and 2 give the exciplex emission spectra from the pyrene-dimethylaniline and the anthracene-dimethylaniline systems respectively in n-heptane, benzene, *p*-xylol and mesitylene for which the  $\epsilon = n^2$  relation holds. It may be observed that in aromatic solvents the exciplex emission is considerably red shifted compared with that in n-heptane. The peak positions of exciplex emission in different solvents are summarized in Table 1.

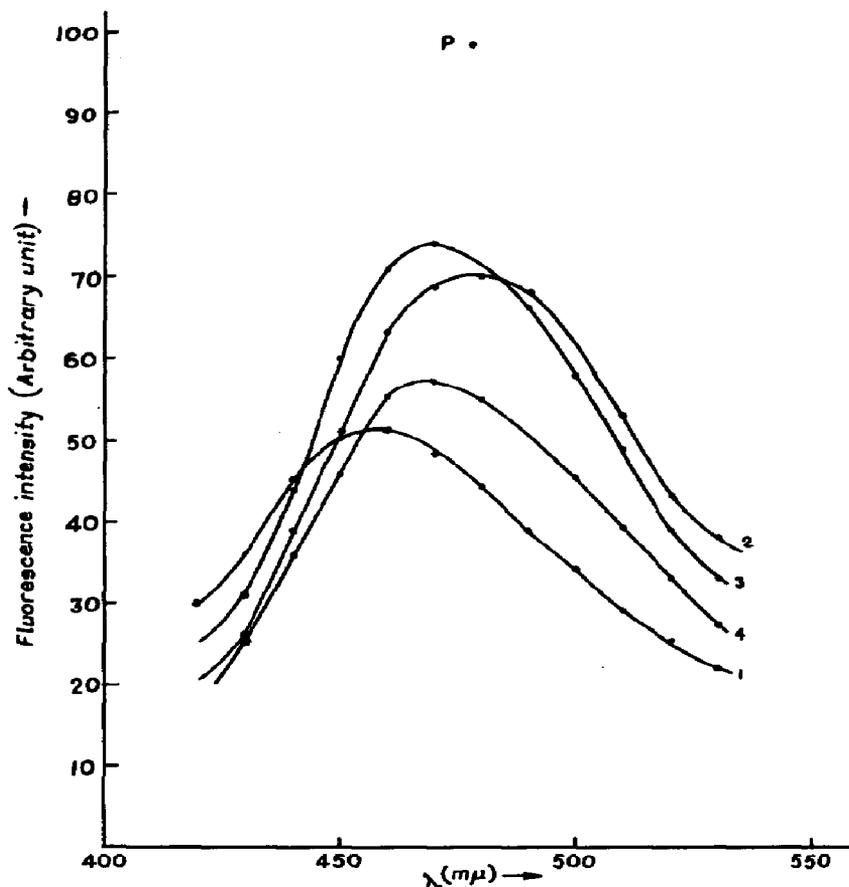
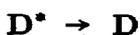


Fig. 1. Emission spectra of  $2.33 \times 10^{-3}$  M pyrene and 0.6 M dimethylaniline in (1) n-heptane, (2) benzene, (3) *p*-xylol and (4) mesitylene.

The exciplex emission spectrum from the pyrene-dimethylaniline system in n-heptane containing different amounts of benzene is shown in Fig. 3. The intensity of exciplex emission increases with increasing benzene concentration and there is an isosbestic point at 430 nm. This appears to indicate that there is only one new species with a maximum emission frequency around 480 nm, *i.e.* the peak in pure benzene. Because of this finding the fluorescence transformation of Fig. 3 may be attributed to a reaction of the following type which takes place during the lifetime of the exciplex:



$$K = \frac{[DA^*]}{[D^*][A]}$$

$$k_f [D^*]$$

$$k_f' [DA^*]$$

$$k_q [D^*]$$

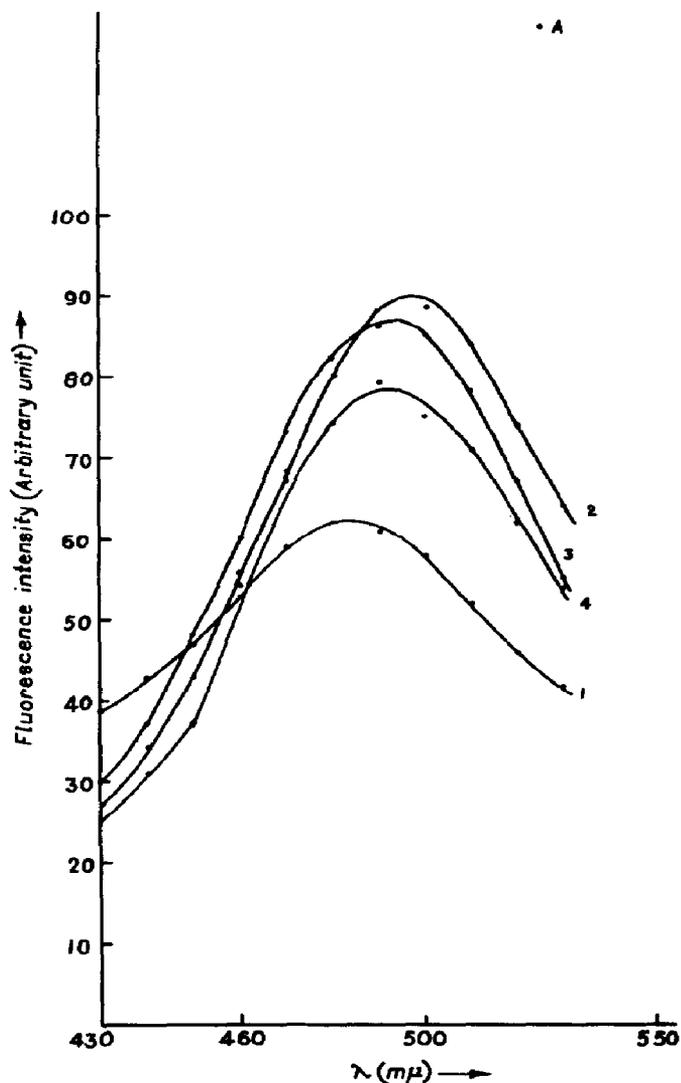


Fig. 2. Emission spectra of  $0.9 \times 10^{-3}$  M anthracene and 0.6 M dimethylaniline in (1) n-heptane, (2) benzene, (3) *p*-xylol and (4) mesitylene.



$$k'_q [DA^*]$$

where  $[D^*]$  and  $[A]$  stand for exciplex and benzene concentration respectively. From the above scheme the following simple relation can be derived for the relative fluorescence intensity  $f$  of the solution in which the concentration of benzene is  $[A]$ ,  $f_0$  being the intensity in pure n-heptane:

$$\frac{1 - f_0/f}{[A]} = -K + \alpha K \frac{f_0}{f} \quad (1)$$

where

TABLE 1

Exciplex emission in different solvents

Exciplex	Solvent	$\epsilon^{20^\circ\text{C}}$	$n_D^{20^\circ\text{C}}$	$\lambda_{\text{max}}$ (nm)
Pyrene ( $2.33 \times 10^{-3}$ M)– dimethylaniline (0.6 M)	n-heptane	1.93	1.388	460
	benzene	2.28	1.498	480
	p-xylol	2.24	1.495	470
	mesitylene	2.28	1.499	468
Anthracene ( $0.9 \times 10^{-3}$ M)– dimethylaniline (0.6 M)	n-heptane	1.93	1.388	485
	benzene	2.28	1.498	498
	p-xylol	2.24	1.495	492
	mesitylene	2.28	1.499	490

$\epsilon$  and  $n$  values were taken from International Critical Tables.

$$\alpha = \frac{\phi'}{\phi} \quad \phi' = \frac{k'_t}{k'_t + k'_q}$$

$$\phi = \frac{k_t}{k_t + k_q}$$

From the linear plot of

$$\frac{1 - f_0/f}{[A]} \text{ vs. } \frac{f_0}{f}$$

the equilibrium constant  $K$  for exciplex–benzene complex formation may be obtained. Figure 4 gives such a plot for the pyrene–dimethylaniline system in n-heptane containing 1.6–7.2 M benzene. It may be observed that the plot is fairly linear. Table 2 gives the equilibrium constants, estimated graphically, for pyrene–dimethylaniline and anthracene–dimethylaniline with benzene, p-xylol and mesitylene.

TABLE 2

Equilibrium constants for exciplex–aromatic complex formation

Exciplex	Aromatic	$K (\text{M}^{-1}) \times 10^2$
Pyrene–dimethylaniline	benzene	6.1
	p-xylol	5.8
	mesitylene	4.4
Anthracene–dimethylaniline	benzene	5.4
	p-xylol	6.0
	mesitylene	1.0

It appears that in these systems we have exciplex–aromatic complex formation similar to the triple exciplex studied by Beens and Weller [6]. The

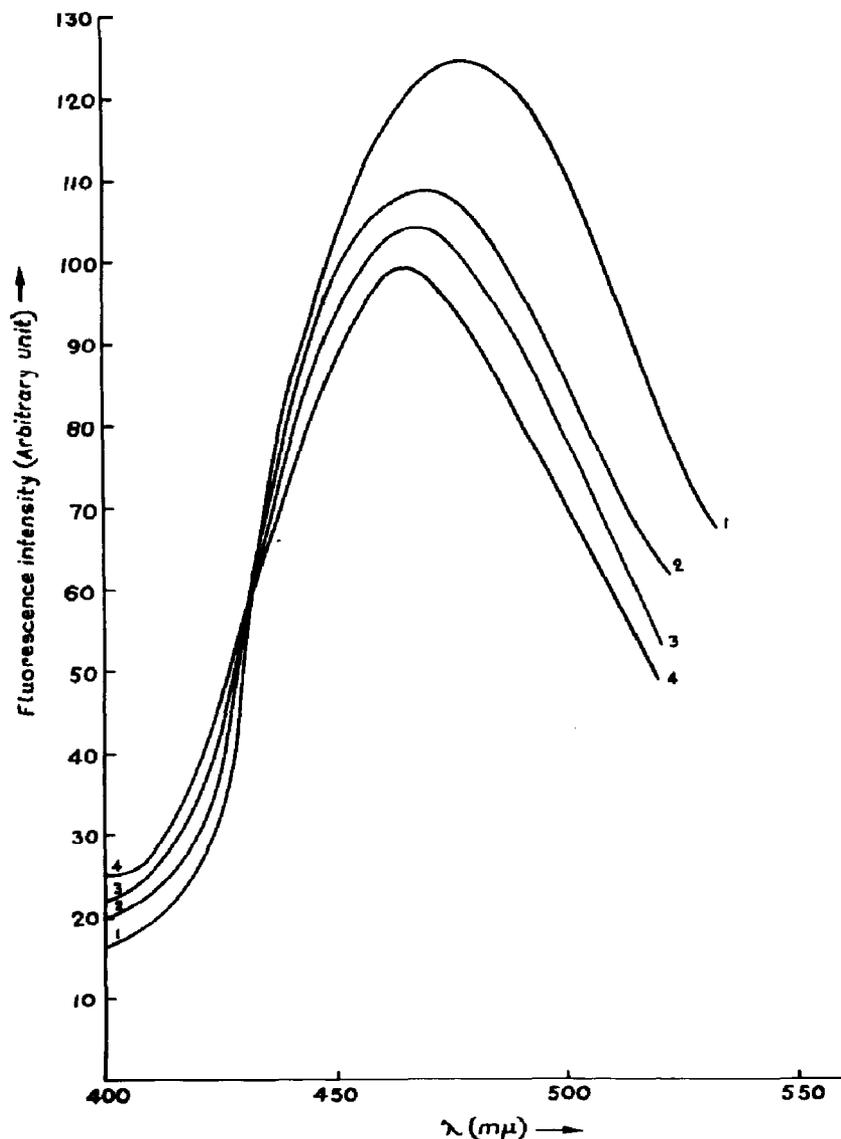


Fig. 3. Emission spectra of  $2.33 \times 10^{-3}$  M pyrene and 0.6 M dimethylaniline in n-heptane where the concentration of benzene is (1) 7.2 M, (2) 5.87 M, (3) 3.2 M and (4) 1.6 M.

question that now arises is: are the aromatics acting as donors or acceptors? The ionization energies of benzene, *p*-xylol and mesitylene are 9.245 eV, 8.445 eV and 8.400 eV respectively [7]. In the simple donor-acceptor interaction model we expect that the red shift should be in the order mesitylene > *p*-xylol > benzene. The reverse appears to be the case. It has been proposed that in these excited state interactions the sum of the ionization energy and the electron affinity of the partners determines the direction and energy of electron transfer [4]. In the absence of reliable values for electron af-

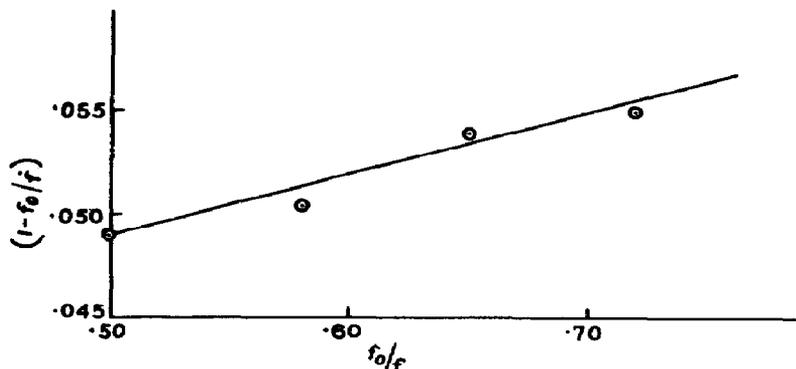


Fig. 4. Verification of relation (1) from the data in Fig. 3.

finities of benzenoid hydrocarbons this point could not be tested. It is desirable to extend this study to a few more exciplexes in order to establish the generality or specificity of the observed effect.

## References

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