THE EFFECT OF SOLVENT ON EXCIPLEX EMISSION FROM PYRENE–TRIBUTYLAMINE AND ANTHRACENE–TRIBUTYLAMINE SYSTEMS

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Summary

The exciplex emissions from the pyrene–tributylamine (TBA) and anthracene–TBA systems have been found to undergo a red shift in solvents of higher dielectric constants. From these shifts it has been estimated that the extent of charge transfer is 66% in the pyrene–TBA system, while it is over 80% in the anthracene–TBA system. In aromatic hydrocarbon solvents the exciplex emission was found to undergo a red shift and an intensification in the order benzene > p-xylene > mesitylene. This has been attributed to triple exciplex formation, for which the equilibrium constants between the exciplex and the aromatic solvents have been found to be 3.2×10^{-2} (benzene), 2.2×10^{-2} (p-xylene) and 2.2×10^{-2} (mesitylene) for the pyrene–TBA system, while for the anthracene–TBA system the equilibrium constants were 8.3×10^{-3} (benzene) 8.3×10^{-3} (p-xylene) and 6.6×10^{-3} (mesitylene). A tentative explanation for the effect of aromatic hydrocarbon solvents on exciplex emission has been suggested.

In alcoholic solvents the exciplex emissions were blue shifted owing to the formation of hydrogen bonded complexes between the exciplex and the alcohols. The pyrene–TBA system forms much stronger hydrogen bonds with alcohols than the anthracene–TBA system. This was considered to indicate the participation of the lone pair electrons at the nitrogen of TBA in hydrogen bond formation.

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1. Introduction

In the study of solvent effect on exciplex emission from pyrene–dimethylaniline (DMA) and anthracene–DMA systems, it has been observed that these exciplexes enter into a specific donor–acceptor type of interaction with aromatic hydrocarbons and hydroxylic solvents [1]. It was assumed that in these exciplexes DMA acts as an n-donor to the excited pyrene and anthracene molecules. In order to account for the orientation effect in nucleophilic substitution, organic chemists have assumed that the non-bonding lone pair electrons at the nitrogen atom in DMA may be donated to

the π electron system of the phenyl ring, *i.e.* the so-called mesomeric inter-action may take place between n and π electrons in DMA. The question is, what role, if any, does such a mesomeric effect play in the formation of exciplexes and in the interaction of solvents with exciplexes. With a view to throwing light on this aspect of the problem the previous studies were extended to pyrene–tributylamine (TBA) and anthracene–TBA systems, since TBA can act solely as a n-donor with no possibility for any mesomeric interaction. The results are reported in the present communication.
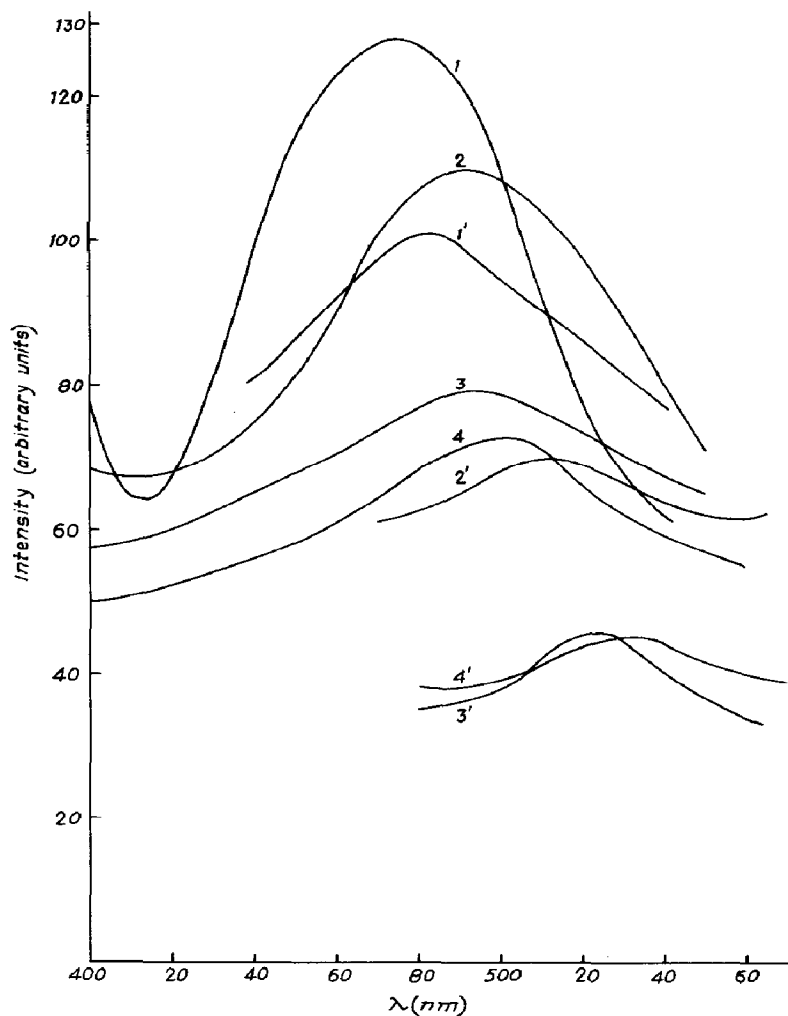

Fig. 1. Exciplex emissions from the pyrene $(2.2 \times 10^{-3}$ M)–TBA (0.7 M) system in heptane (1), chloroform (2), butyl acetate (3) and ethyl acetate (4), and the anthracene $(1.6 \times 10^{-3}$ M)–TBA (0.7 M) system in heptane (1'), butyl acetate (2'), ethyl acetate (3') and methyl acetate (4').

2. Experimental

The solvents and all other chemicals used were carefully purified and dried following the recommended procedure. All of them were subjected to a final chromatographic separation procedure. The solutions were freshly prepared and degassed. Fluorescence measurements were made on a right-angle scattering set-up using 1 cm silica cells. The exciting light was the 3650 Å mercury line isolated from a North Holland Phillips high pressure mercury arc using a set of two Baird Associate interference filters. The emitted light was allowed to pass through a Beckman Model DU monochromator and the intensity of the light was measured on a d.c. amplifier used in conjunction with a 931 A RCA photomultiplier tube. The intensity of the incident beam was monitored on an attenuated beam using a similar detection system. The phototubes were maintained at a low temperature to minimize noise.

3. Results

Exciplex emissions from pyrene–TBA and anthracene–TBA in four different solvents were recorded. The emissions were found to consist of a broad structureless band, the peak position of which was shifted to longer wavelengths in solvents of higher dielectric constants. The intensity of the emission was unaffected by the TBA concentrations in the range 0.1 - 1.0 M. The spectra are given in Fig. 1 and the relevant data are summarized in Table 1.

TABLE 1

Exciplex emission from the pyrene–TBA and anthracene–TBA systems in different solvents

| Exciplex	Solvent	n	ϵ	$\dfrac{\epsilon-1}{\epsilon+2} - \dfrac{n^2-1}{n^2+2}$	Exciplex emission		μ_e (debye)
					λ (nm)	$h\nu$ (eV)	
Pyrene	chloroform	1.442	4.72	0.289	493	2.53	10.1
$(2.1 \times 10^{-3}$ M)	butyl acetate	1.394	5.01	0.333	498	2.50	
–TBA (0.7 M)	ethyl acetate	1.370	6.02	0.399	505	2.47	
	n-heptane	1.388	1.93	0.000	475	2.63	
Anthracene	butyl acetate	1.394	5.01	0.333	510	2.44	12.5
$(1.8 \times 10^{-3}$ M)	ethyl acetate	1.370	6.02	0.399	523	2.39	
–TBA (0.7 M)	methyl acetate	1.362	6.70	0.435	536	2.35	
	n-heptane	1.388	1.93	0.000	480	2.63	
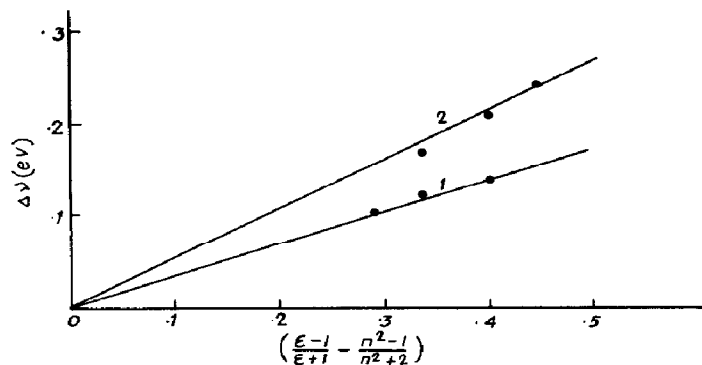
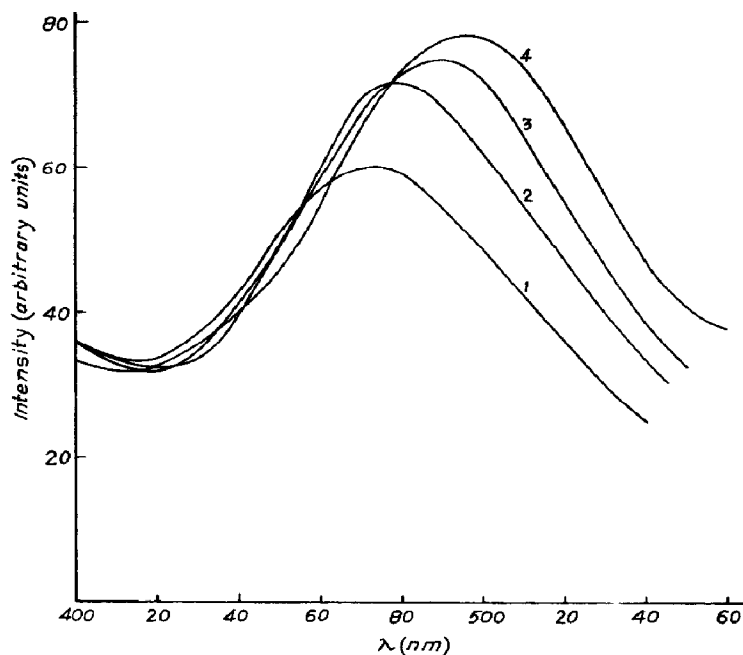Fig. 2. Spectral shift with reaction field strength: 1, the pyrene–TBA; 2, the anthracene–TBA.

Fig. 3. Exciplex emission from the pyrene–TBA system in heptane (1), mesitylene (2), p-xylene (3) and benzene (4).

When $h\Delta\nu$ was plotted against

$$\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2}$$

for each system, perfectly linear curves were obtained (Fig. 2); $\Delta\nu$ for n-heptane was taken as zero.

Figures 3 and 4 display the exciplex emission spectra of the pyrene–TBA and anthracene–TBA systems in benzene, p-xylene and mesitylene. In these solvents the intensity of the exciplex emission was higher than that in

n-heptane and the peak position shifted to longer wavelengths in the order benzene > *p*-xylene > mesitylene.

In alcoholic solvents the spectrum of the pyrene–TBA system was markedly different from that of the anthracene–TBA system. In the pyrene–TBA system the peak positions were located in the range of 445 - 460 nm in n-propyl, sec-butyl and tert-butyl alcohol which were at shorter wavelengths than that in n-heptane while for the anthracene–TBA system the emissions from alcohols were located at 500 nm, *i.e.* at a longer wavelengths than that from n-heptane (Figs. 5 and 6). The emission from n-propyl and n-butyl alcohol appeared at the same position. In both of these systems the emission was strongly quenched and the quenching followed the order primary > secondary > tertiary.

4. Discussion

The concentration-dependent association of aromatic hydrocarbons and amines giving rise to broad structureless emission on the longer wavelength side of the characteristic fluorescence of the hydrocarbon has been ascribed to charge transfer complex (exciplex) formation between the hydrocarbon in the excited state and the amine in the ground state [2 - 4]. The following simple energy level scheme may be proposed for the exciplex emission process [1]:
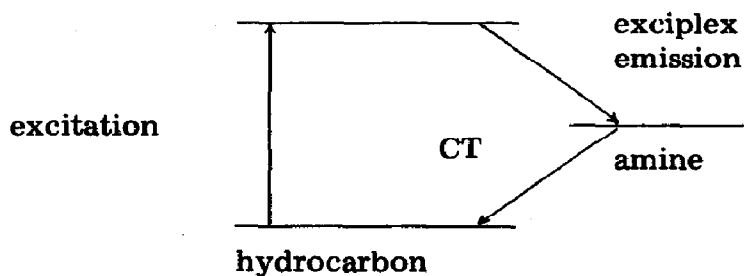
In a mixture of pyrene and TBA or anthracene and TBA, structureless emission was observed in the range 470 - 480 nm, when the hydrocarbon was excited [2]. This emission may be associated with exciplex emission since no ground state association of the hydrocarbon and amine could be detected from absorption spectral data. Since charge transfer complexes are dipolar, it was surmized that the exciplexes will also be dipolar. The dipole moment may be estimated from the spectral shift in the emission spectrum in solvents of higher dielectric constants using Onsager's reaction field concept [1, 5]. According to Onsager's theory of liquid dielectrics, the energy change associated with the transfer of a dipole from vacuum to a medium of dielectric constant ϵ and refractive index n is given as

$$\Delta E = \frac{\mu^2}{a^3} \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right)$$
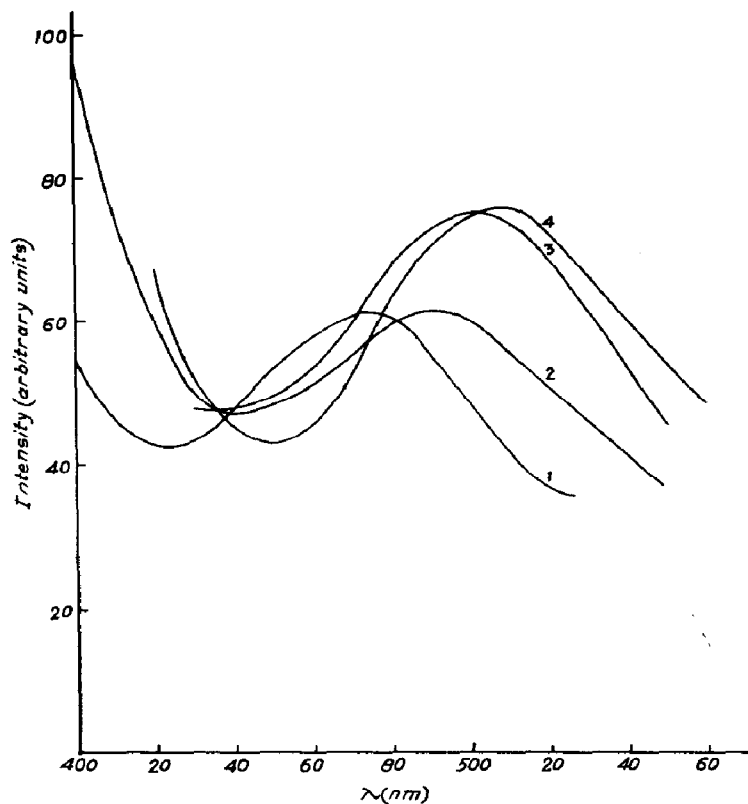
Fig. 4. Exciplex emission from the anthracene–TBA system in heptane (1), mesitylene (2), p-xylene (3) and benzene (4).

where a is the radius of a spherical cavity surrounding the molecule. Hence, if we know the emission frequency in vacuum and in the medium of dielectric constant ϵ and refractive index n, then the energy difference $h\Delta\nu$ will be related to ΔE by

$$h\Delta\nu = \Delta E$$

A plot of

$$h\Delta\nu \; versus \; \frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2}$$

should be linear, as is found to be the case in Fig. 2. The dipole moments calculated from the slope taking a as 4 Å are given in Table 1. Since complete charge transfer gives a dipole moment of 15.3 debye, it is estimated from the dipole moment values in Table 1 that the extent of charge transfer is 66% for the pyrene–TBA complex but 80% for the anthracene–TBA complex. It was observed for pyrene–DMA and anthracene–DMA complexes that the extent of charge transfer was 80% in both cases [1]. No satisfactory explanation can be suggested to account for this difference in behaviour of TBA and DMA systems.
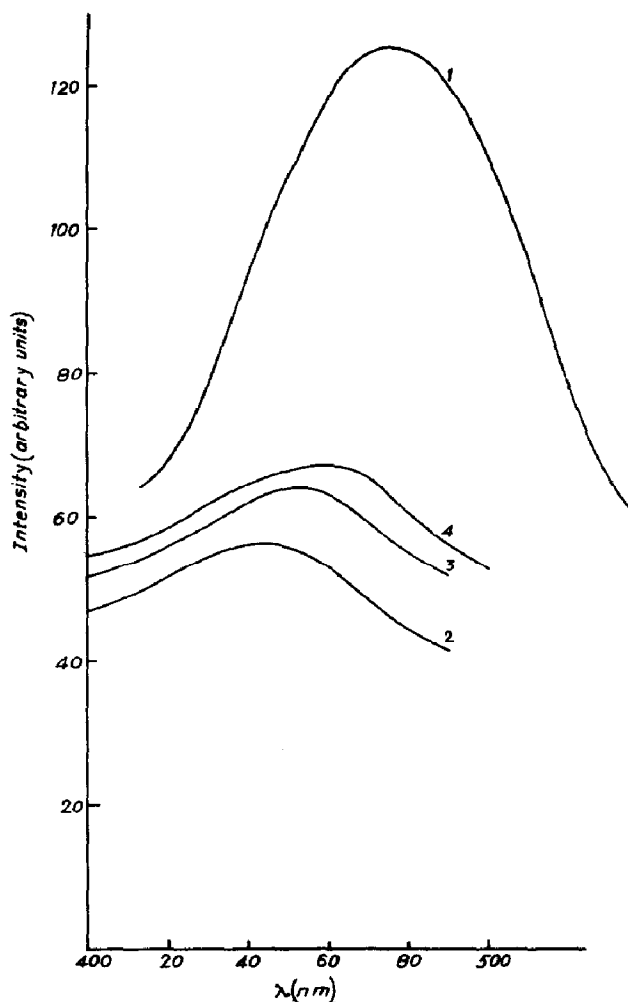
Fig. 5. Exciplex emission from the pyrene $(2.2 \times 10^{-3}$ M)–TBA (0.7 M) system in heptane (1), n-propanol (2), sec-butanol (3) and tert-butanol (4).

From what has been said earlier it is obvious that solvents which have

$$\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} = 0$$

i.e. for which $\epsilon = n^2$, the exciplex emission should appear at the same position as that in n-heptane. From Figs. 3 and 4 it may be observed that the exciplex emissions from the pyrene–TBA and anthracene–TBA systems are considerably red shifted in benzene, p-xylene and mesitylene for which the relation $\epsilon = n^2$ holds. As the benzene concentration is increased the exciplex emission intensity from the pyrene–TBA and anthracene–TBA systems is increased with respect to that in heptane. The same situation is encountered with two other aromatic solvents. This effect of aromatic solvents has also been observed with pyrene–DMA and anthracene–DMA systems and has been
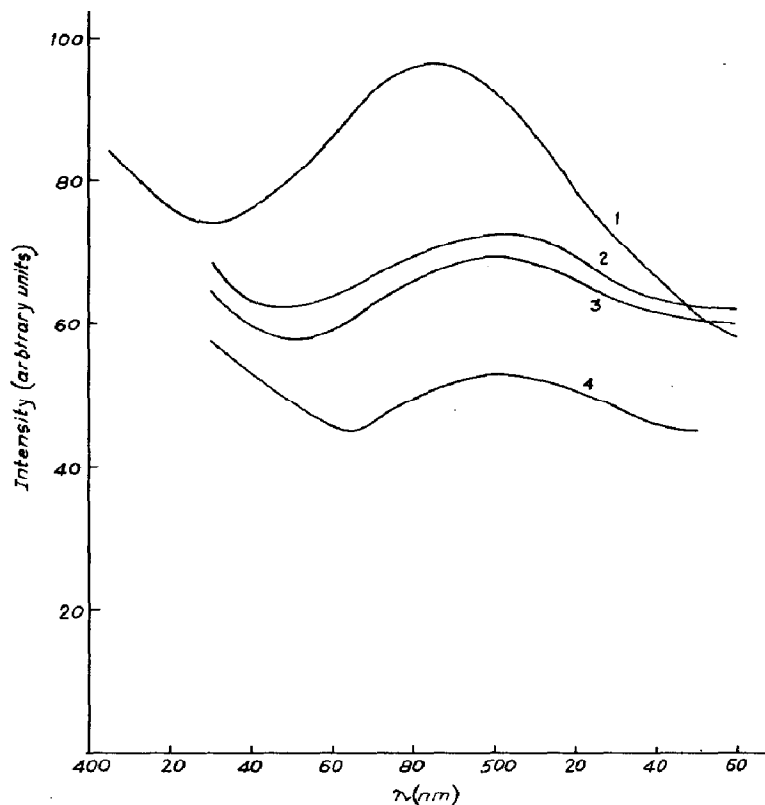
Fig. 6. Exciplex emission from the anthracene (1.6 × 10^{-3} M)–TBA (0.7 M) system in heptane (1), n-propanol (2), sec-butanol (3) and tert-butanol (4).

attributed to triple exciplex formation between the exciplex and the aromatic hydrocarbon. The equilibrium constant for 1:1 complex formation between the exciplex and the aromatic hydrocarbon may be estimated from the relation [1]

$$\frac{f/f_o - 1}{[A]} = \alpha K - K \frac{f}{f_o}$$

$$\alpha = \frac{\text{yield for triple exciplex}}{\text{yield for exciplex}}$$

where f is the fluorescence intensity of the exciplex in heptane containing [A] M of aromatic hydrocarbon and f_o is the intensity in pure heptane. The plot of $(f/f_o - 1)/[A]$ versus f/f_o was fairly linear (Fig. 7) and from the slope of this the equilibrium constants for triple exciplex formation were estimated. The relevent data are given in Table 2.

The equilibrium constants for triple exciplex formation are higher by an order of magnitude for hydrocarbon–DMA systems than for hydrocarbon–TBA systems, as may be observed by comparing the previously reported data [1] with the values given in Table 2.
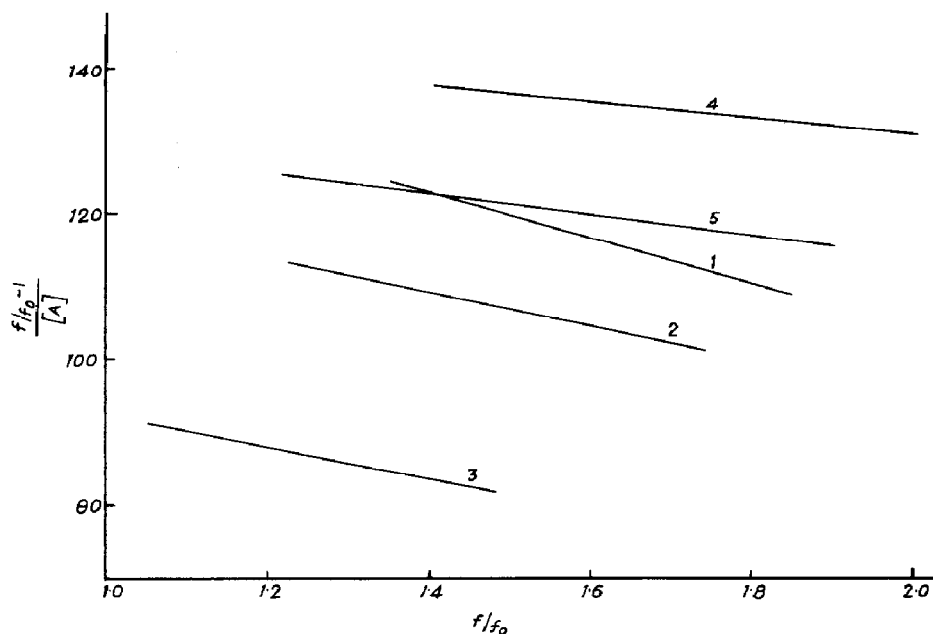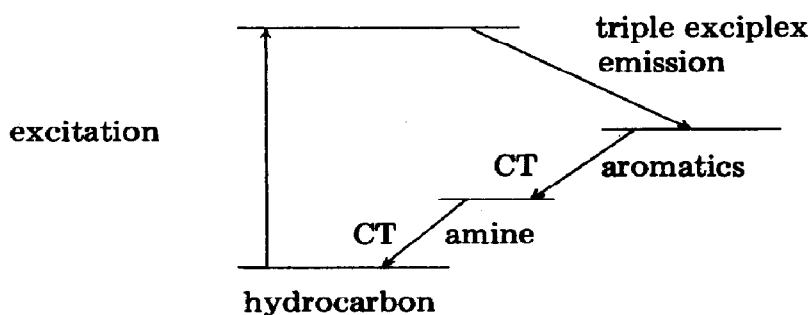
Fig. 7. Exciplex–aromatic complex formation of the pyrene–TBA system with benzene (1), p-xylene (2), mesitylene (3), and of the anthracene–TBA system with benzene (4) and p-xylene (5).

Beens and Weller [3] proposed that in triple exciplexes the exciplex acts as the acceptor and the aromatic as the donor in an electron transfer process. The ionization energies of benzene, p-xylene and mesitylene are respectively 9.245 eV, 8.445 eV and 8.400 eV. In the charge transfer absorption process it is known that as the ionization energy of the donor is reduced the absorption band shifts to longer wavelengths. The reverse appears to be the case for the emission process. On retaining the Been and Weller [3] model for triple exciplexes, this effect may be understood using the following energy level scheme:

It may be observed that, as the ionization energy of the aromatics is reduced, the triple exciplex emission frequency is increased, i.e. the observed blue shift effect.

TABLE 2

Equilibrium constants for triple exciplex formation

Exciplex	Aromatics A	[A] (M)	f/f_o	λ_{max} (nm)	K (M^{-1})
Pyrene (3.2×10^{-3} M) −TBA (0.7 M)	benzene	6.52 4.89 3.96	1.74 1.57 1.48	500	3.2×10^{-2}
	p-xylene	4.76 3.07 2.39	1.51 1.34 1.28	490	2.2×10^{-2}
	mesitylene	4.28 1.91 1.08	1.36 1.22 1.12	480	2.2×10^{-2}
Anthracene (2.2×10^{-3} M) −TBA (0.7 M)	benzene	6.52 4.89 3.96	1.87 1.68 1.54	510	8.3×10^{-3}
	p-xylene	6.52 4.89 3.96	1.77 1.58 1.50	500	8.3×10^{-3}
	mesitylene	4.28 1.91 1.08	1.18 1.08 1.05	490	6.6×10^{-3}

What could be the structure of the triple exciplexes? We may ascribe to the pyrene−TBA exciplex and the pyrene−TBA−benzene triple exciplex the following structures: $Py^{-}-TBA^{+}$ and $Py^{-}-TBA-Bz^{+}$. These models clearly predict a higher dipole moment for the triple exciplex than the pyrene−TBA exciplex. If this contention is justified then the triple exciplex emission peak should show a stronger red shift in mediums of higher dielectric constant than the pyrene−TBA exciplex. Figure 8 gives the emission from the pyrene−TBA−benzene exciplex in heptane, butyl acetate and ethyl acetate. The triple exciplex emission is very strongly quenched by high dielectric solvents but the large red shift expected for a triple exciplex is not observed. Much more work is needed in this field before the whole situation can be clarified.

Alcohols form hydrogen-bonded complexes with amines through the lone pair non-bonding electrons at the nitrogen atom. In alcoholic solutions the n-donor energy levels of the amines should be lowered and consequently the exciplex emission should show a blue shift compared with that in n-heptane solution. In the pyrene−TBA system the exciplex emission is strongly blue shifted as expected (Fig. 5) and the high dielectric constants of the alcohols fail to cause the expected red shift. In the pyrene−DMA system, although the blue shift effect of the alcohols was present, the red shift effect due to high dielectric constants was quite considerable, causing the
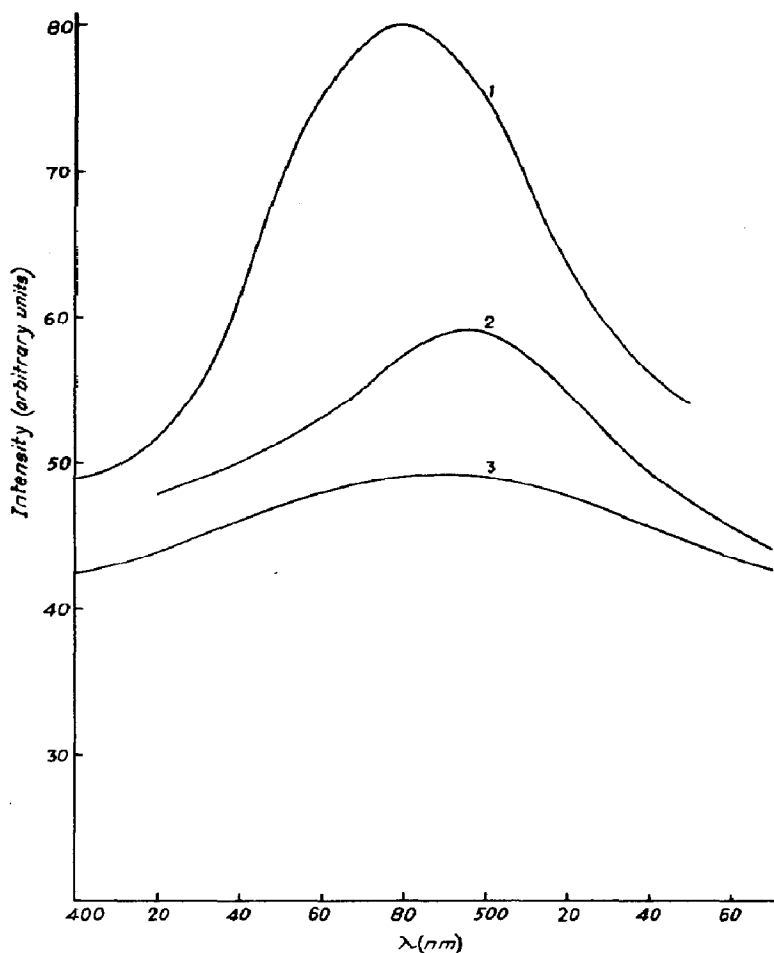
Fig. 8. Emission spectra of the pyrene $(2.2 \times 10^{-3}$ M)–TBA (0.7 M)–benzene (2.39 M) system in heptane (1), butyl acetate (2) and ethyl acetate (3).

emission band to appear red shifted from that in n-heptane. For the anthracene–TBA system (Fig. 6), the exciplex emission in primary, secondary and tertiary alcohols appeared at 500 nm. The alcohols have dielectric constants in the range 10.9 - 20.1 but the exciplex emission peak appeared at shorter wavelengths than that in butyl acetate which has a dielectric constant of only 5.01. Thus the blue shift effect of alcohols is operative for the anthracene–TBA system but the red shift effect due to the higher dielectric constants of alcohols is superimposed on it, causing the exciplex emission to appear red shifted from that in n-heptane solution.

What could be the reason for the characteristic difference in the effect of alcohols on the exciplex emission from the pyrene–TBA and anthracene–TBA systems? We propose the following tentative explanation. The extent of charge transfer in exciplex formation is 66% for the pyrene–TBA system but 80% for the anthracene–TBA system. Since the non-bonding lone pair electrons are involved in the charge transfer process, the lone pair electron

density at the amine nitrogen is higher in the pyrene–TBA complex than that in the anthracene–TBA complex. As the lone pair electrons are responsible for the formation of hydrogen bonds between the amines and the alcohols, we may conclude that hydrogen bonding is stronger for the pyrene–TBA complex than for the anthracene–TBA complex and that consequently the blue shift is greater for the pyrene–TBA complex than for the anthracene–TBA system.

Using time-resolved fluorescence studies on exciplexes, Nakashima *et al.* [2] have shown that the exciplex formation process in the case of aromatic hydrocarbon–aliphatic amine systems is much slower than that for the systems with aromatic amines. They have attributed this to a structural change in the aliphatic amine on exciplex formation. They assumed that the pyramidal structure of the aliphatic amine changes to a planar structure on exciplex formation. This interpretation, however, cannot explain why the pyrene–TBA system differs so markedly from the anthracene–TBA system in the extent of the electron transfer process and in the effect of hydroxylic solvents.

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