

## Short Communication

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### Quenching of 2-ethoxynaphthalene fluorescence by methyl benzoate: fluorescence enhancement at higher quencher concentrations

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Fluorescence quenching by foreign substances has attracted considerable interest in recent years. Of the mechanisms of fluorescence quenching, charge transfer or electron transfer has perhaps been the most extensively studied [1 - 10]. We have previously studied [7] the quenching of 2-ethoxynaphthalene (2-EN) fluorescence by *m*-dimethylphthalate (*m*-DMP) and the solvent dependence of the stability of the exciplex formed in that system. It was concluded that the exciplex formed with 2-EN and *m*-DMP can be characterized as a "weak" exciplex in which the contribution of the charge transfer configuration is relatively small. In this work we report the quenching of 2-EN fluorescence by methyl benzoate (MB). This system shows an unusual behaviour in the region of higher concentrations of MB.

Quenching of 2-EN fluorescence by MB is not efficient and more than  $1 \text{ mol l}^{-1}$  of MB is required for quenching to be apparent. The absorption spectrum of 2-EN recorded in cyclohexane is structured. On the addition of a few moles per litre of MB, these structures are somewhat blurred and, at the same time, the spectrum slightly shifts to the red. However, even in neat MB the spectrum is very similar to those obtained in other solvents such as benzene, *N,N*-dimethylformamide (DMF) etc. This indicates that the quenching is dynamic in nature, *i.e.* there is no ground state complex which is responsible for the quenching.

Figure 1 shows Stern-Volmer plots of the quenching in cyclohexane. Dissolved oxygen was removed from the sample by bubbling nitrogen gas before measurement. It should be noted that the MB concentration of  $8.0 \text{ mol l}^{-1}$  corresponds to neat MB. Although very weak, exciplex fluorescence is detected on the lower wavenumber tail of the unquenched fluorescence. It can be seen in Fig. 1 that the quenching is more efficient at lower temperatures. This may indicate that dissociation of the exciplex to excited 2-EN and MB prevails in this temperature region.

Figure 2 shows the quenching in DMF. It can be seen that the quenching occurs more efficiently than in cyclohexane. Furthermore, a maximum

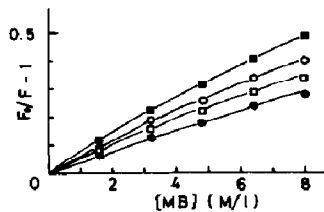


Fig. 1. The quenching of 2-EN fluorescence by MB in deoxygenated cyclohexane:  $\bullet$ , at 45 °C;  $\square$ , at 35 °C;  $\circ$ , at 25 °C;  $\blacksquare$ , at 15 °C.

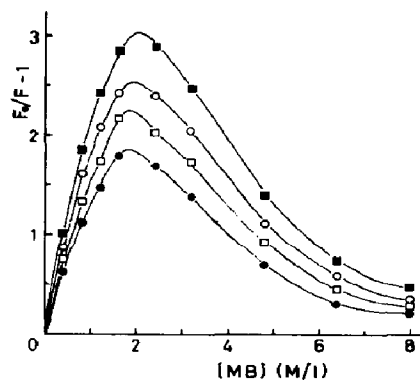
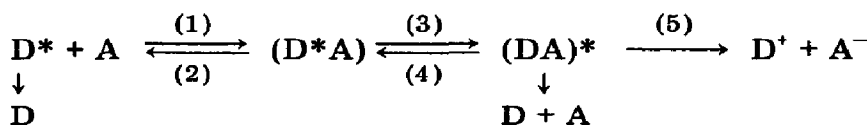


Fig. 2. The quenching of 2-EN fluorescence by MB in deoxygenated DMF:  $\bullet$ , at 45 °C;  $\square$ , at 35 °C;  $\circ$ , at 25 °C;  $\blacksquare$ , at 15 °C.

is reached at an MB concentration of about  $2 \text{ mol l}^{-1}$  and further addition of MB reduces the quenching. In other words, fluorescence is enhanced rather than quenched at higher concentrations of the quencher. Again the temperature effect shows that exciplex dissociation prevails. A similar result was obtained when acetonitrile was used as solvent, although the quenching was somewhat more efficient. This can be attributed to the lower viscosity of this solvent.

It is thought that there has been only one previous report on this kind of unusual quenching curve. Sveshnikoff has reported a similar behaviour for rhodamine B in ethanol-nitrobenzene mixtures, and has suggested that a molecular complex formed with ethanol and nitrobenzene molecules could be responsible for the quenching [11, 12]. In the present case, however, participation of such a complex in the quenching seems unlikely, since a result similar to that shown in Fig. 2 was also obtained in acetonitrile.

The quenching scheme is represented as follows:



where  $(D^*A)$  and  $(DA)^*$  denote the encounter complex and the exciplex respectively. Recalling that both DMF and acetonitrile are highly polar (with dielectric constants of 36.5 and 37.5 respectively at 20 °C), the quenching curve shown in Fig. 2 may be interpreted as follows. At lower concentrations of MB, process (5) is efficient and the fluorescence is quenched in the usual manner. Further addition of MB (dielectric constant, 6.6 at 20 °C) lowers the polarity of the solvent mixture (MB-DMF or MB-acetonitrile). The photophysical properties of the exciplex are largely affected by the change

TABLE 1

Exciplex fluorescence yield (relative) as a function of MB concentration

Concentration of MB (mol l <sup>-1</sup> )	Fluorescence yield	Concentration of MB (mol l <sup>-1</sup> )	Fluorescence yield
0.8	1/50	3.2	1/20
1.2	1/50	4.8	1/8
1.6	1/50	6.4	1/2
2.4	1/20	8.0 (neat)	1

The solvent used was DMF.

in solvent polarity. Process (5) in the scheme is particularly sensitive to solvent polarity and its rate decreases on going from polar to less polar solvents. This increases the quantum yield of process (4) and consequently the fluorescence of D\* is enhanced rather than quenched at higher MB concentrations.

Table 1 shows the relative values of the exciplex fluorescence yield. These values are not very accurate, because the exciplex fluorescence is very weak. However, it is clear from Table 1 that the exciplex fluorescence yield increases with increasing MB concentration. In addition, the maximum of the exciplex fluorescence shifts largely to the blue with increasing MB concentration. These observations can also be attributed to the lower polarity of the MB-DMF mixture.

It is to be noted that in DMF or acetonitrile, even at the lowest concentration of MB studied, process (4) is efficient to some extent, since quenching shows a negative temperature dependence. Thus process (5) is not very efficient even in highly polar solvents. This is in contrast with almost all other exciplexes reported hitherto. This may be attributed to the weaker charge transfer interaction between excited 2-EN and MB [7].

In summary, it is concluded that MB acts not only as a quencher but also as a substance that lowers the polarity of the solvent mixture. The properties of the exciplex are largely affected by added MB and as a result the fluorescence quenching is depressed in spite of the higher concentrations of the quencher.

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