

NOTA

THE ABSORPTION AND EXCITATION SPECTRA OF 2-ETHYLNAPHTHALENE IN SOLUTION

Following excitation into higher excited singlet states of fluorescent aromatic molecules it has generally been assumed that they return to the first excited singlet state through a rapid, radiationless, internal conversion (1). As a consequence, the fluorescence quantum yield should be independent of the wavelength of the radiation used for excitation (2). This has been verified in most cases (3) although a few exceptions have been reported in the past (4, 5, 6).

LIPSKY and co-workers (7, 8) presented a detailed study of the variation of the quantum yield with exciting wavelength for benzene, toluene, *p*-xylene and mesitylene. The quantum yield was found to be lower in the regions of high molar extinction coefficient. These results were confirmed and extended to naphthalene and some of its derivatives (1,6 dimethylnaphthalene, 2-methylnaphthalene and fluoronaphthalene) (9, 10). For all cases an effect

of concentration was observed, the magnitude of the effect decreasing with decreasing concentration, except for benzene, where it increases upon dilution by an inert solvent.

In recent work on this effect (11, 12, 13, 14) use has been made of binary systems where the fluorescence emission comes from an adequate solute (e. g. 2,5 diphenyloxazole or naphthyl-2-phenyl-5-oxazole-1,3) of higher quantum efficiency than that of the molecules whose internal conversion properties are under study. In this case there is an additional process to be taken into account, namely the solvent-solute energy transfer. And, since the energy donor molecules are excited into higher excited singlet states, some authors have pointed out that these higher excited states may be involved in the energy transfer process (14, 15, 16, 17).

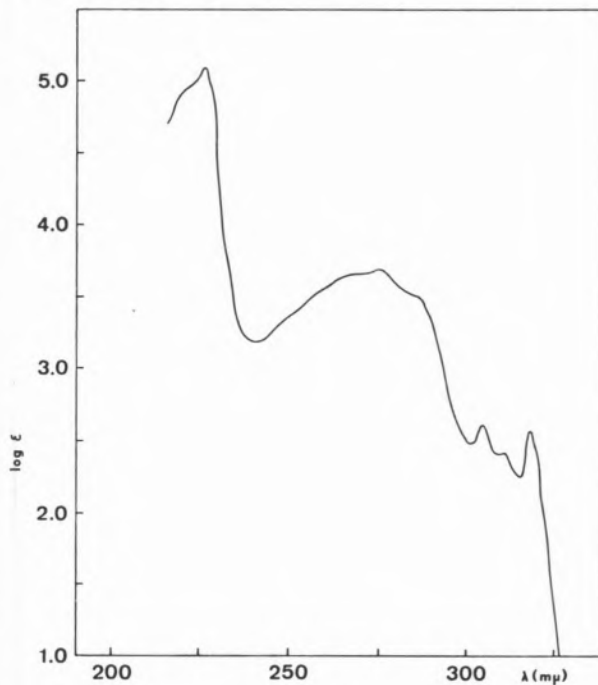


Fig. 1

Absorption spectrum of 2-ethylnaphthalene (solvent cyclohexane)

As a preliminary account of an extensive study of this problem which is being undertaken at this laboratory the present Note reports on another system for which the internal conversion is not unity for all exciting wavelengths and concentrations. Fig. 1 shows the absorption spectrum of 2-ethylnaphthalene (puriss. from Aldrich, Co) obtained with solutions in cyclohexane. Fig. 2

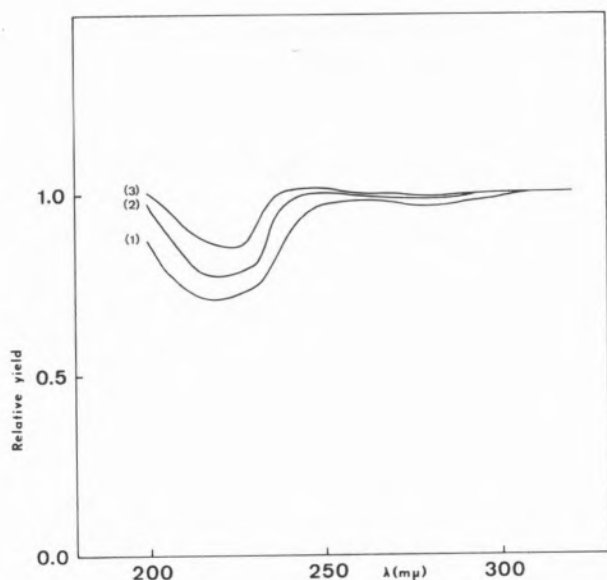


Fig. 2

Excitation spectra of de-oxygenated 2-ethylnaphthalene solutions in cyclohexane: (1) 6.5M (pure 2-ethylnaphthalene); (2) 3.2M; (3) 1.6M

shows the excitation spectra of several de-oxygenated solutions of 2-ethylnaphthalene in cyclohexane. Fig. 3 shows the excitation spectra of the same solutions containing oxygen at atmospheric pressure. These spectra have not been corrected for reflectivity losses (8, 9, 11). The error in the measurements is estimated to be of the order of 10 %.

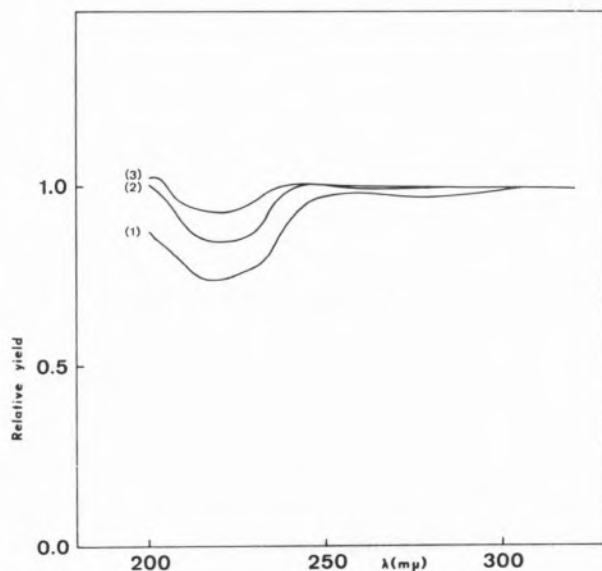


Fig. 3

Excitation spectra of air-equilibrated 2-ethylnaphthalene solutions in cyclohexane: (1) 6.5M (pure 2-ethylnaphthalene); (2) 3.2M; (3) 1.6M.

The following points are to be noted. As with other naphthalene derivatives there is a broad correlation between the excitation spectra and the absorption spectrum, the magnitude of the effect being greater in the region of high molar extinction coefficient. Dilution with an inert solvent, transparent to the exciting radiation, tends to reduce the effect. The presence of oxygen also reduces the effect. The absorption spectrum is similar to that of other naphthalene derivatives.

A detailed analysis of these results as well as those obtained with binary systems where 2-ethylnaphthalene is used as an energy donor will be presented in a later publication.

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