Solvent Effects on the Spectral Properties of the Methine Dyes

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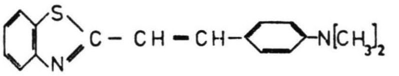
The spectral characteristics (absorption, fluorescence and lifetimes of fluorescence) of methine dyes in different solvents are presented. The results show that the methine dyes in polar solvents emit a dual fluorescence. From the dependence of the fluorescence spectrum on the dye concentration it is suggested that excimer formation is responsible for the second band of fluorescence.

Introduction

Recently, methine dyes have attracted interest for their possible application in display devices [1, 2]. A liquid crystal display based on the ability of "guest" pleochroic dyes to align parallel to the "host" liquid crystal was first described by Heilmeier and Zanoni [3]. Since then the basic properties of "guest-host" type liquid crystal display devices and the effects of various parameters on their colour display properties have been clarified [1, 2]. Unfortunately, the main theoretical problems concerning the molecular interactions between the liquid crystal matrix and the dye molecules remain still open [4, 5]. The present study deals with the spectral effects of solvation, complexation and aggregation of two representative methine dyes.

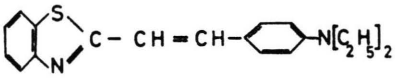
Material and Methods

The methine dyes used were



I

and



II

The dyes were synthesized as already described [6]. The compounds were thoroughly identified and purified. The absorption spectra were measured with an UV-VIS Zeiss spectrophotometer. The fluorescence emission was excited at 405 nm with an interference filter [5.5 nm bandwith]. The experimental arrangement for the fluorescence measurements was described elsewhere [7]. The fluorescence lifetimes were measured with a phase shift fluorometer [8].

Results and Discussion

As can be seen from Table I, the spectral parameters of absorption and emission of the dyes I and II are quite similar. Therefore, Figs. 1 and 2 show only the absorption and emission spectra of dye II. The absorption spectra of both compounds are only slightly influenced by the type of solvent (Fig. 1 and Table 1). On the other hand the emission spectra in polar solvents differ remarkably in the position of the maxima and the shape of the spectra. The emission spectra are shifted towards longer wavelengths as the polarity of the solvent increases. The shape of the emission band is strongly dependent on the kind of solvent. In the polar solvents the emission spectra exhibit a second fluorescence band with a maximum at about 538 nm (Figure 2). In this case the emission spectra are composed of two bands with maxima at 508 and 538 nm (Fig. 2; curve B).

The slight changes in the absorption spectra as well as the observation that the emission spectra are broadened by polar solvents (Table 1) could be simply explained in terms of solut-solvent interactions [9, 10], whereas the nature of the dual fluorescence has recently been the subject of considerable controversies [11].

Lippert, Lüder and Boos [12] discovered that p-cyano-N, N dimethylaniline exhibits two fluorescence bands. From the solvent shifts it was evident that the low energy fluorescence emitting state was highly polar. Lippert et al. [12] ascribed the dual fluorescence to an inversion of states, ^1L_a and ^1L_b

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Table 1. Spectral parameters of absorption and emission of methine dyes.

Type of solvent	Dye	Position of maxima absorption nm	Position of maxima fluorescence nm	halfwidth of abs. nm	halfwidth of fluor. nm	Stokes shift nm	Lifetime of fluorescence measured for both maxima	Lifetime of fluorescence measured for second maxima
Benzene	I	397	485	81	44	88	0.5 ns	—
	II	397	485	81	44	88	0.5 ns	—
Methanol	I	406	508, 538	76	73	102	1.0 ns	1.5 ns
	II	406	508, 538	76	73	102	1.0 ns	1.5 ns

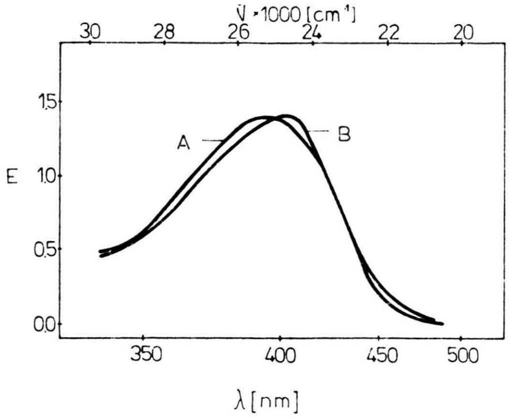

Fig.1. Absorption spectra of dye II in benzene (A) and methanol (B).

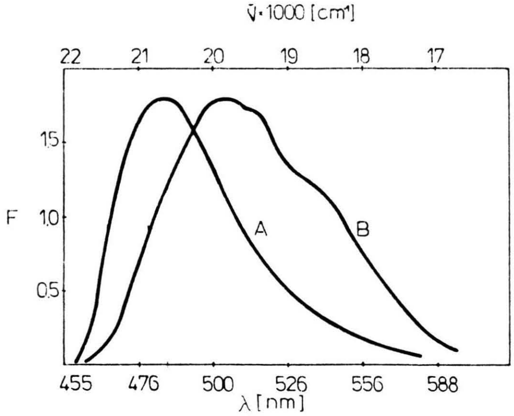

Fig. 2. Fluorescence spectra of dye II in benzene (A) and methanol (B).

in Platt's classification [13], whereby the much more polar ^1L_b state would be stabilized by reorientation of the polar surroundings. According to their assignment, the transitions should be mutually perpendicularly polarized. Since then many new experimental data have been collected and other possible explanations for the dual fluorescence have been suggested: 1) a polar solvent assisted isomerisation of the excited molecule via internal rotation of the $N(CH_3)_2$ and $N(C_2H_5)_2$ group [11]. 2) A stepwise formation of excited complexes with the solvent molecules [14]. 3) A protonation of excited species [14]. 4) An excimer formation [14].

With the aim of understanding the nature of the two excited states involved in our case the following experiments were carried out: 1) We have found that both emission bands have the same excitation spectra, e.g. both emission bands result from the lowest singlet-singlet transition. 2) Our unpublished results on those dyes in liquid crystal matrixes suggest that the transition moments responsible for the two emission bands are rather mutually parallel polarized. This invalidates the hypothesis of a solvent-induced inversion of electronic states of different polarity [12]. 3) The idea of possible protonation of the excited species has been checked by addition of small amounts (3%) of 10N KOH to water alcoholic solvents. The addition of KOH did not change the intensities of both maxima, which excludes the protonation hypothesis. 4) In order to check the excimer hypothesis the dependence of the intensities of the two emission bands on the concentration of the dye has been studied. The results are shown in Figs. 3 and 4. Figure 3 shows the dependence of the ratio of the intensities of the two maxima of the fluorescence bands (F_{508}/F_{538}) on the concentration of the dye. A relative increase of the intensity of the second band (with maximum at 538 nm) of both compounds with higher concentrations is observed. This is especially true for dye II (Fig. 3; curve II). Figure 4 shows the whole spectrum of dye II in methanol for pigment concentrations of the order 10^{-2} M. It should be pointed out that we could not find any relative changes in the absorption spectra in this range of dye concentrations. Therefore, the above results strongly suggest

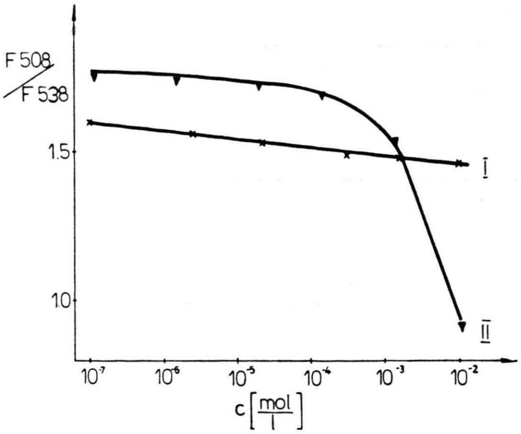

Fig. 3. The dependence of the relative intensities of the two fluorescence maxima on the concentration of the pigments in methanol.

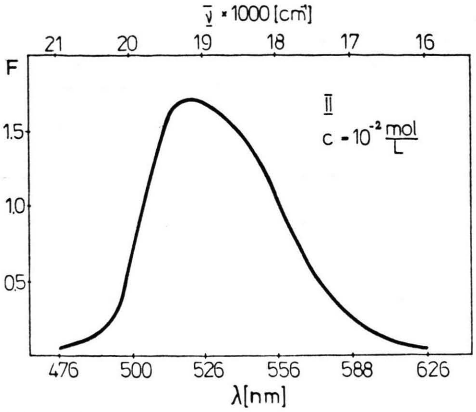

Fig. 4. Fluorescence spectrum of dye II in methanol at high concentration of the pigment ($c = 10^{-2}$ M).

that excimer formation is mainly responsible for the observed dual fluorescence.

The high energy band (maximum at 508 nm) is due to molecular fluorescence and has a very short lifetime ($\tau = 0.5$ ns Table 1). The low energy band (maximum at 538 nm) is due to excimer fluorescence and has a longer lifetime ($\tau = 1.5$ ns Table 1). This second band occurs in polar solvents only.

Unfortunatly, some questions remain still open. Among them, the most important are:

1) Why does the excimer formation occur only in polar and not in nonpolar solvents?
2) How much does the internal rotation of the $N(CH_3)_2$ or $N(C_2H_5)_2$ groups contribute to the observed dual fluorescence?

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