EFFECT OF SOLVENT REORIENTATION RELAXATION ON THE LUMINESCENCE PROPERTIES OF DYES IN RIGID MATRICES

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The delayed fluorescence and phosphorescence of different dyes in rigid matrices were found to depend strongly on the exciting wavelength between 77 and 350 K, exciting at the long wavelength edge of the absorption spectrum. We conclude that this phenomenon can be explained by the reorientation relaxation process of the solvating shell.

Introduction

The maxima of prompt fluorescence (F) and delayed emission (DE) (*i.e.* delayed fluorescence DF, phosphorescence Ph) spectra of certain organic compounds (dyes, arylethylenes, quinine derivatives *etc.*) dissolved in *polar solvents* are found to be shifted to longer wavelength, while the half-width of the luminescence bands is slightly decreasing with exciting wavelength (λ_{ex}) increased continuously from the center of the absorption band [1, 3, 5]. On the other hand, the fluorescence and phosphorescence maxima of the solutions excited at the center of their absorption band are shifted to shorter wavelength, and at the same time their half-widths are decreasing with decreasing temperature (T) 300 K through 77 K [3, 5]. These phenomena can be explained only by a model in which dissolved dipol molecules and their solvating shells are taken into account together (creating an *elementary entity*; further on we use this term) for discussing luminescence spectra since there is a strong interaction between the solute molecule and the sorrounding solvent molecules. Moreover the solute molecules in polar solvents form a number of differently solvated species.

In the elementary entities the orientation of the solvent molecules is different. In the solution the different elementary entities have different interaction energy both in the ground and the excited state so that the electron energy states of the solvated system are not only vibrationally but also orientationally broadened, and for this reason the states have been termed *orientation-dependent vibronic* energy states [2, 6].

Both in the ground and the excited state there are *equilibrium* and *non-equilibrium* states (the latter in excited state is a Franck-Condon state, FC), and the energy distribution of elementary entities are different amoung these states. The distribution depends on solvent orientation, excitation energy (ν_{ex}) and very strongly on temperature. So in the excited state (and in the ground one as well) a (slow or rapid) reorientation process takes place.

The factor $f=\tau_r/\tau$ can characterise how the orientation-dependent vibronic energy state is realised in equilibrium or non-equilibrium. (τ_r is the solvent reorientation relaxation time which depends strongly on viscosity, *i. e.* the time which is needed to achieve the equilibrium state from a non-equlibrium state; τ is the decay time of emission.)

Recent studies on the *edge-excitation red shift* (this nomenclature was introduced in [3]) were reported mostly separately for fluorescence and phosphorescence, respectively. Here we report on the various kinds of photoluminescence (F, DF, Ph) with particular emphasis on the extremes when $\tau_F \ll \tau_{Ph}$ and $\tau_r \gg \tau_F$, and at the same time, $\tau_r > \tau_{Ph}$ (*e.g.* $T=77$ K) and $\tau_r < \tau_{Ph}$ (*e.g.* $T=250$ K), respectively. For our investigations we choose dipol dye molecules in rigid polar matrix.

Experimental

The emission (F, DF, Ph) and absorption spectra of erithrosin B and eosin Y dissolved in polyvinyl alcohol (PVA) glycerol, EPA and polymethyl methacrylate (PMMK) were measured as described elsewhere [5, 6]. We shall mainly confine the discussion to those results obtained with $1 \cdot 10^{-3}$ g/g erythrosin B and eosin Y in PVA.

Results

As shown in Fig. la the maxima of the prompt fluorescence of erythrosin B in PVA (λ^{F}_{max}) at room and low temperature were at the same wavelength. However the peak positions of delayed fluorescence (λ^{DF}_{max}) and phosphorescence (λ^{Ph}_{max}) exhibited a blue shift on freezing the solution, using the same excitation (Fig. 1b).

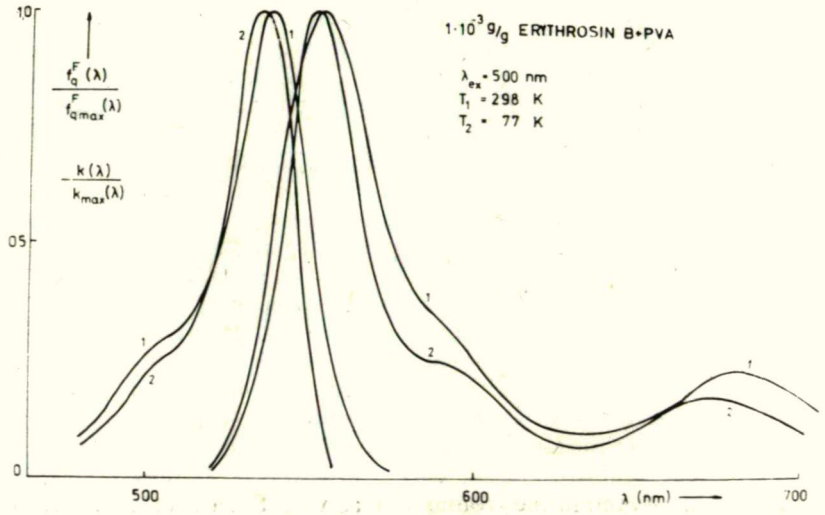

Fig. 1a. Erythrosin B in PVA: the normalized absorption and total emission spectra

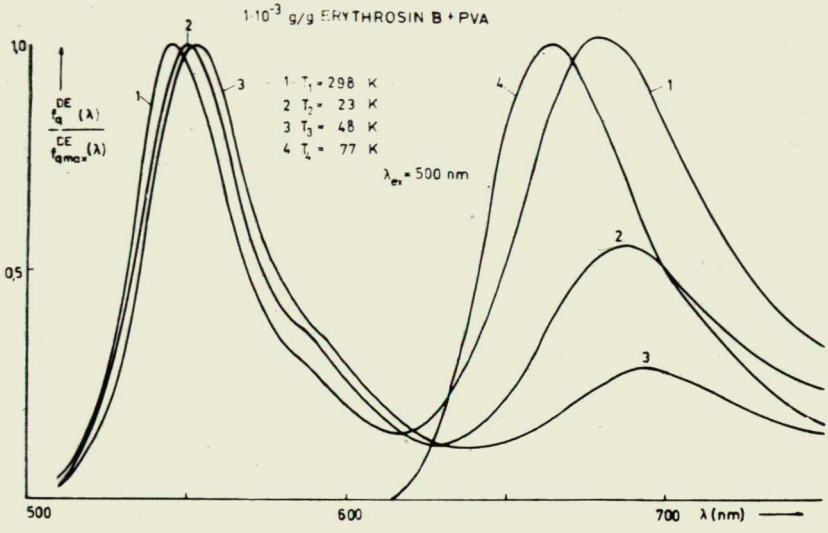

Fig. 1b. Erythrosin B in PVA: delayed emission (DF and Ph) spectra normalized at the DF peak at high and low temperature.

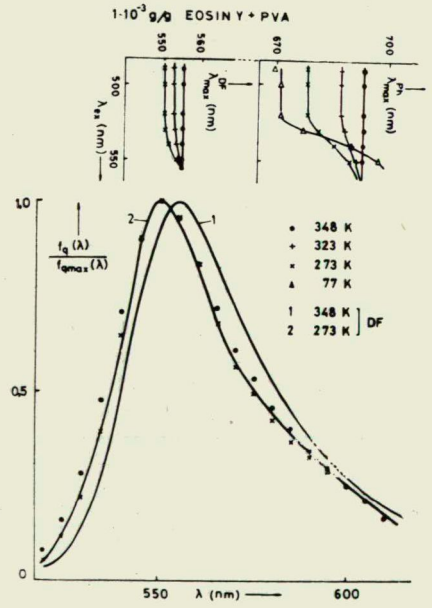

Fig. 2. Eosin Y in PVA: the normalized prompt and delayed fluorescence spectra, the peak positions of DF and Ph are also indicated.

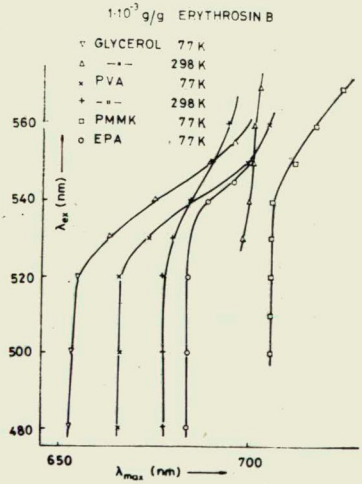

Fig. 3. The excitation energy dependence of the peak positions for the Ph spectra of erythrosin B dissolved in different solutions.

In the case of eosin Y in PVA the F ($T=298-348$ K) and the DF ($T=298$ K) peak positions were the same ($\lambda_{ex}=500$ nm) and were observed at shorter wavelength as compared to the maximum of DF using 500 (or 555) nm excitation ($T=348$ K) (Fig. 2).

Peak positions of DF and Ph of eosin Y in PVA are shown in Fig. 2. In Fig. 3 the Ph maxima of erythrosin B in various matrices are shown which depend on the λ_{ex} both at low and high temperatures. The shift reached a limit at $T=298-348$ K with PVA matrix, however, the limit was at another wavelength if $T=77$ K. Fig. 4 shows the absorption and the Ph spectra of erythrosin B in PVA at 298 and 77 K. In the case of glycerol this limit in the shift of Ph maximum was approximately the same, although the difference of peak positions was 50 nm using center excitation. The low temperature phosphorescence of erythrosin B in EPA and PMMK also depended on the excitation.

Discussion

From our experimental results on peak positions (Fig. 2) we have obtained for the f factor with a reasonable approximation (Eq. (11) of [4]) a value of 3—0.3 ($T=298$—348 K). It follows then that $\tau_r \sim 3$—0.3 msec since $\tau_{Ph} \sim 1$ msec. Thus the following relations hold $\tau_F \ll \tau_r$ (323 K) $< \tau_{Ph} \sim \tau_{DF} < \tau_r$ (298 K).

On the basis of these data we shall explain our experimental results in terms of relaxation processes. The total fluorescence and phosphorescence spectrum is composed from a number of spectra originating from the emission of different elementary entities. If the ν_{ex} is sufficiently high, each elementary entity is excited, whereas if the ν_{ex} is at low level, only a part of elementary entities is excited, so that the lower wavelength side of the resultant total emission is gradually fallen behind. Therefore, it seems reasonable to use the representation given in Fig. 4 where the long wavelength edges of the Ph spectrum due to various excitation are fitting one on the other.

We can explain the results as follows:

(1) Since $\tau_F \ll \tau_r$ at every temperature in matrices, the fluorescence emission always originates from non-equilibrium excited singlet states.

(2) Since $\tau_{DF} \sim \tau_{Ph} > \tau_r$ (348 K), the distribution is the same and not far from the equilibrium (quasi-equilibrium) both in singlet and triplet states, when DF and the Ph arise, therefore λ_{max}^{DF} (348 K) $> \lambda_{max}^{F} > \lambda_{max}^{DF}$ (298 K).

(3) At 77—298 K we may write $\tau_{Ph} \ll \tau_r$(77—298 K), and thus Ph results from a partially non-equilibrium distribution ($T>77$ K), and is entirely due to non-equilibrium triplet state at 77 K with every excitation. The observed peak position limits in PVA probably refer to different kind of elementary entities which are present at 77 K but are indistinguishable at higher temperatures.

From the model presented we conclude that the fluorescence of the dyes in rigid matrices should strongly depend on excitation, and that the excitation at the bulk of absorption should lead to a time-dependent red shift of fluorescence and phosphorescence (if $f>1$).

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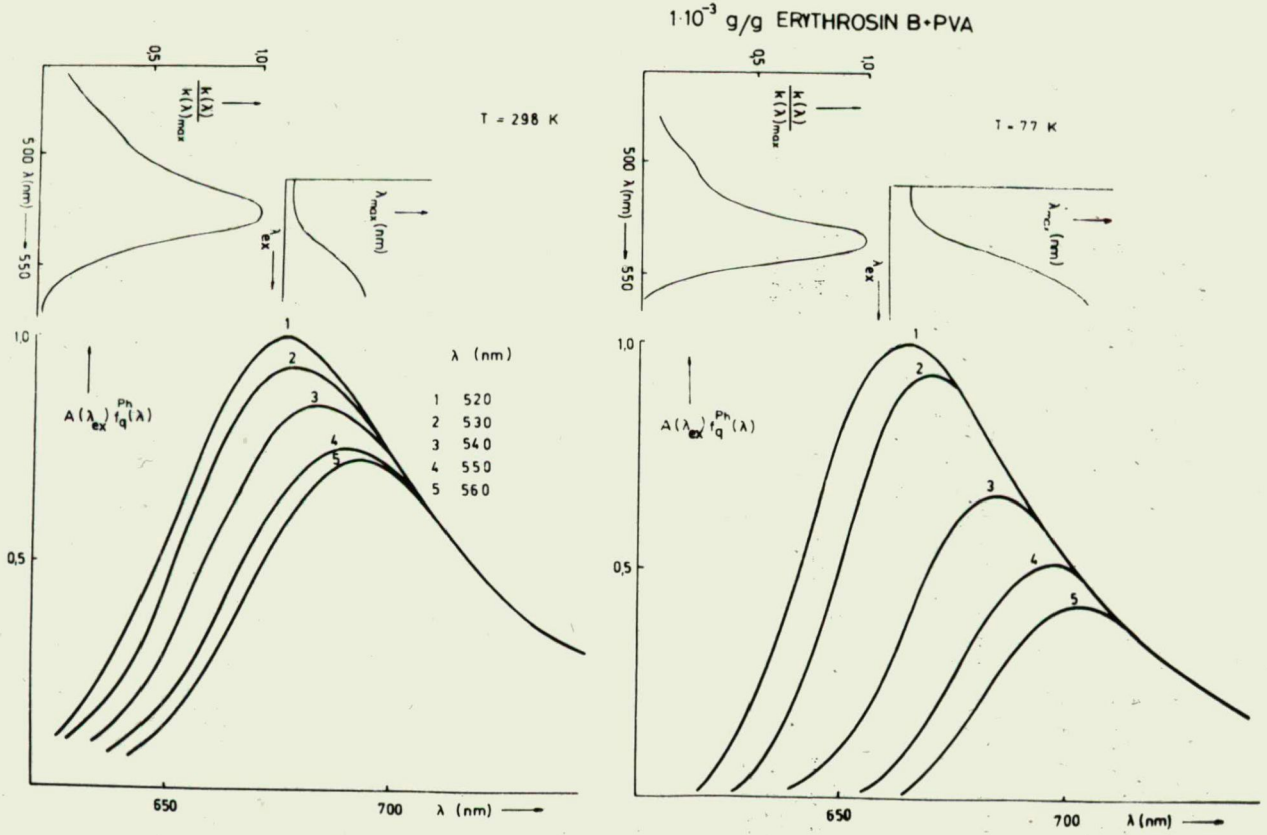

Fig. 4. The absorption and the relative phosphorescence spectra of erythrosin B and the Ph peaks plotted against the wavelength of excitation.

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ВЛИЯНИЕ РЕОРИЕНТАЦИОННОЙ РЕЛАКСАЦИИ РАСТВОРИТЕЛЯ НА ЛЮМИНЕСЦЕНТНЫЕ ОСОБЕННОСТИ КРАСИТЕЛЕЙ В ТВЁРДЫХ МАТРИЦАХ

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Найдено, что замедленная термофлуоресценция и фосфоресценция разных красителей в твёрдых матрицах находится в строгой зависимости от длины возбуждающей волны, если возбуждение велось с частотой длиноволнового края спектра, в температурных пределах между 77 и 350 К. Мы пришли к заключению, что явление может объясняться реориентационным релаксационным процессом сольватной оболочки.