

# Molecular Properties of PPO Excimer Luminescence in a Binary Solvent

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Time resolved emission spectra and the luminescence decay of 2,5-diphenyloxazole in dioxane-water mixtures disclose an important influence of water on the observed luminescence. We suppose that this is caused by structural changes of the solution connected with its water content.

**Key words:** Luminescence, Excimers, TRES, Emission spectra, Solution structure.

Investigations of the electronic energy transfer in the radioluminescence of dioxane-water (DW) solutions containing the luminescence probe 2,5-diphenyloxazole (PPO) have revealed the existence of solvent complexes [1–3]. To explain the influence of the solvent complexes on the luminescence probe we have now studied the photoluminescence of PPO solutions in binary DW solvents with water concentrations ranging from 0 to 40 volume-% by measuring the photoluminescence decays and time resolved emission spectra (TRES).

The source of the exciting light pulses with 310 nm wavelength and 12 ps duration was a frequency multiplier excited by light pulses from an argon-dye laser system produced by Spectra-Physics. The fluorescence decays were measured by the time-correlated single photon counting method described in [4].

For solutions with small PPO concentrations ( $4.9 \cdot 10^{-3}$  M/l) and water contents not exceeding 1%, the luminescence spectrum shows only a band of monomer luminescence with the maximum at 370 nm. No evolution of spectra of these solutions was observed (see Table 1).

The increase of water content above 1% at PPO concentration  $\geq 4.9 \cdot 10^{-3}$  M/l evokes, apart from the monomer luminescence band, the appearance of the excimer fluorescence band with the maximum at 460 nm. In these solutions emission spectra evolve, the relative luminescence intensity in the excimer band increasing while the intensity of the monomer band decreases as, e.g., it is shown in Figure 1.

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Table 1. Changes of PPO spectra for extreme concentrations of water and PPO.

H <sub>2</sub> O concentrations	1%	40%	1%	40%
PPO concentrations	$4.9 \cdot 10^{-3}$ M/l		$7.4 \cdot 10^{-2}$ M/l	
Evolution of spectra	no	yes	no	yes
Positions of luminescence band maxima of:				
monomer,	370 nm	370 nm	390 nm	400 nm
excimer		460 nm	470 nm	470 nm

Moreover, in the TRES a shift of the shortwave maximum of the band up to 400 nm with increasing PPO concentration above  $4.9 \cdot 10^{-3}$  M/l is observed (see Table 1). Also, the increase of water concentration at a fixed PPO concentration causes a slight displacement in the longwave direction of the shortwave band in the emission spectra.

The photoluminescence decays of the investigated PPO solutions are generally non-exponential. Those measured at  $\lambda = 360$  nm and  $\lambda = 480$  nm were approximated by two-exponential functions

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2),$$

using the calculation method presented in [4]. The luminescence decay times  $\tau_{1A}$  and  $\tau_{2A}$  as well as  $\tau_{1B}$  and  $\tau_{2B}$  obtained for the decays observed at the wavelengths 360 nm and 480 nm, respectively, depend on the water- and PPO-concentrations in the solutions (see Figs. 2 and 3). The times  $\tau_{1A}$  and  $\tau_{1B}$  of the fast decaying luminescence component appearing at both wavelengths are comparable, and they decrease with increasing concentration of water and PPO. However, in the non-aqueous solutions the increase of PPO

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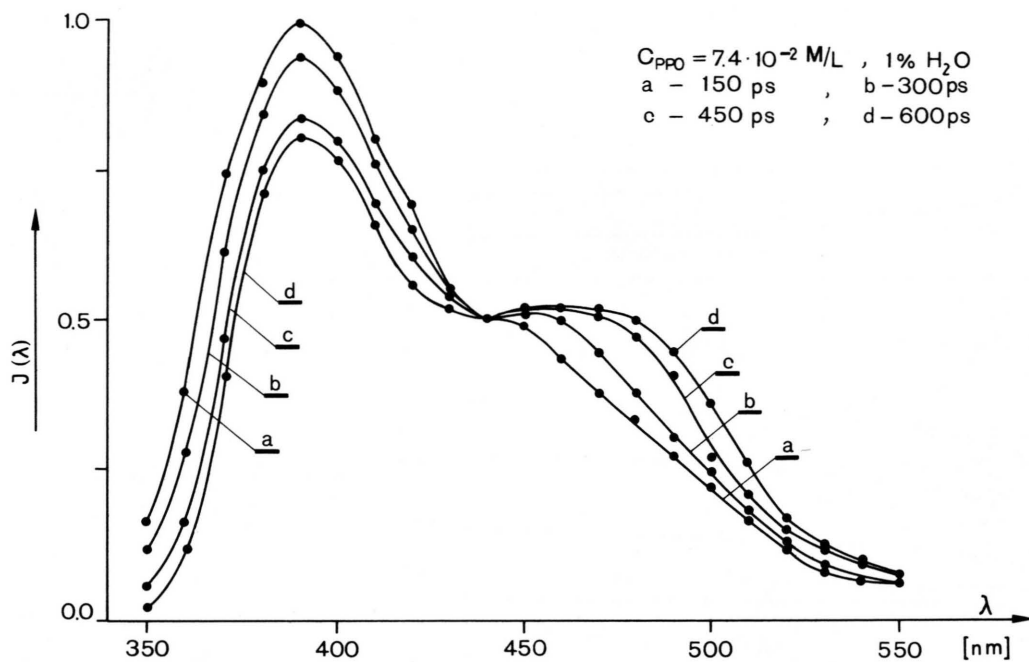
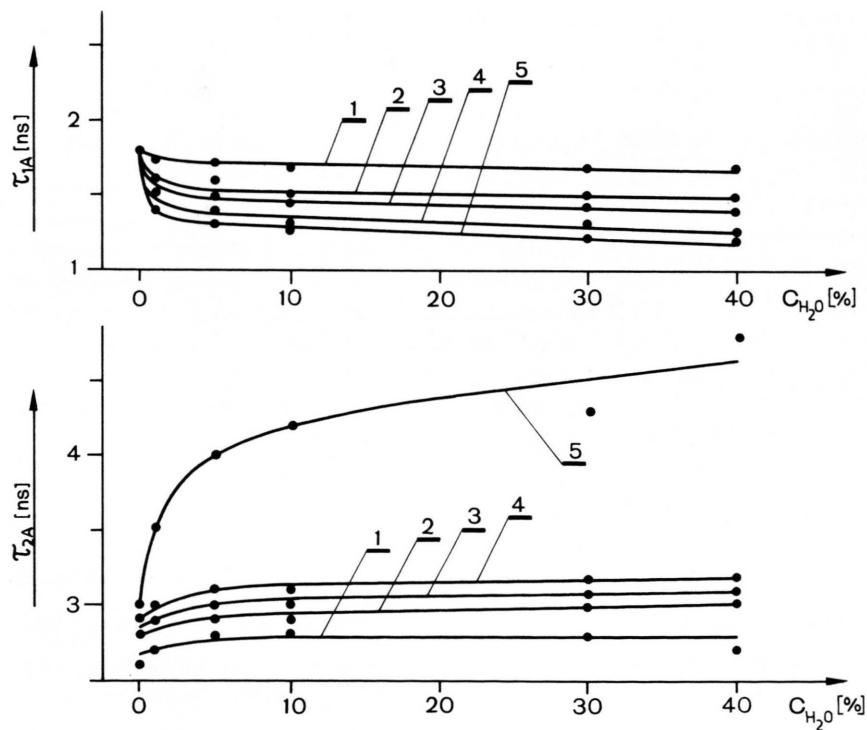


Fig. 1. Time resolved emission spectra of 2,5-diphenyloxazole in binary (dioxane-water) solvent.

Fig. 2. Plots of decay times of the shortlife ( $\tau_{1A}$ ) and longlife ( $\tau_{2A}$ ) components of PPO luminescence observed at  $\lambda_A = 360 \text{ nm}$  versus water concentration. PPO concentration: 1)  $4.9 \cdot 10^{-5} \text{ M/l}$ , 2)  $4.9 \cdot 10^{-3} \text{ M/l}$ , 3)  $2.4 \cdot 10^{-2} \text{ M/l}$ , 4)  $4.9 \cdot 10^{-2} \text{ M/l}$ , 5)  $7.4 \cdot 10^{-2} \text{ M/l}$ .

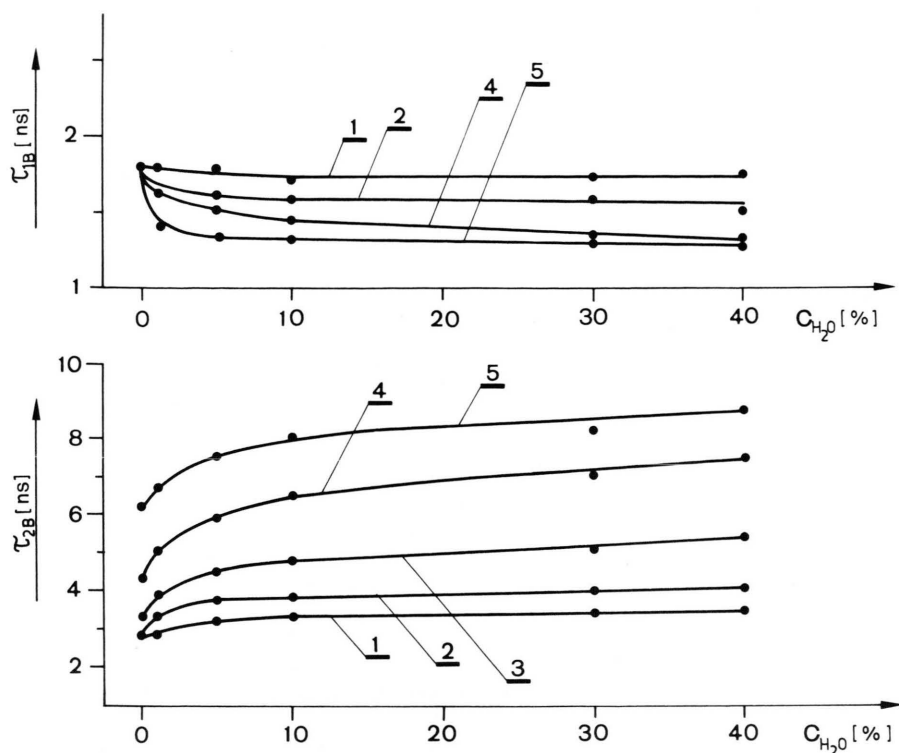


Fig. 3. Plots of decay times of the shortlife ( $\tau_{1B}$ ) and longlife ( $\tau_{2B}$ ) components of PPO luminescence observed at  $\lambda_B = 480$  nm versus water concentration. PPO concentration: 1)  $4.9 \cdot 10^{-5}$  M/l, 2)  $4.9 \cdot 10^{-3}$  M/l, 3)  $2.4 \cdot 10^{-2}$  M/l, 4)  $4.9 \cdot 10^{-2}$  M/l, 5)  $7.4 \cdot 10^{-2}$  M/l.

concentration does not change them. On the other hand, the decay times  $\tau_{2A}$  and  $\tau_{2B}$  of the slowly decaying components become longer with increasing water and PPO concentration. At the same time  $\tau_{2B}$  remains longer in either case, and it increase more than  $\tau_{2A}$  with increase of water and PPO concentration.

The three observations

- influence of water concentration on the luminescence decays,
- dependence of the luminescence decays on the wavelength of the observed light,

- changes of the shortwave band position in the emission spectra of the investigated solutions

cannot be explained in terms of kinetic luminescence theories [5, 6] concerning the existence of the activator (PPO) molecules as monomers and excimers formed in a process controlled by diffusion. It seems that these effects can result from additional physical-chemical processes in binary solvents which may cause the diversity of the structure of monomer and excimer luminescence centres of the probe.

Works on this subject are in progress.

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