PHOTOLUMINESCENCE AND RADIOLUMINESCENCE OF 1,4-DIOXANE–WATER SOLUTIONS OF 2,5-DIPHENYLOXAZOLE

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Summary

It was observed that water has a quenching effect on the radioluminescence of 2,5-diphenyloxazole (PPO)-doped 1,4-dioxane scintillators. Investigations of the photoluminescence decay time and the spectra made it possible to conclude that water stimulates PPO excimerization. The temperature dependence of the radioluminescence efficiency suggests that 1,4-dioxane forms associates with water. The binding energy of 1,4-dioxane–water associates is equal to (0.02 ± 0.005) eV while that of PPO excimers depends on the solvent composition: it is (0.09 ± 0.005) eV in pure 1,4-dioxane and (0.06 ± 0.005) eV in 1,4-dioxane–water mixtures.

1. Introduction

Binary solvent scintillators have been used in the technique of internal counting of low energy radiation [1]. Dioxane–water solutions play an important role in this group of scintillators. However, water reduces the radioluminescence intensity exhibited by dioxane solutions of phenyloxazoles [1 - 3]. This effect is associated with actual quenching of the electronic excitation energy in solutions by water [4].

Hirayama *et al.* [5] showed that water causes red shifting of dioxane luminescence spectra in the vacuum UV region and causes a reduction in its photoluminescence quantum yield. Similarly, water decreases both the radioluminescence intensity of pure dioxane excited with γ radiation and the efficiency of the excitation energy transfer from dioxane to luminescent admixtures [4].

In the investigations of refs. 1 - 5 there is no explanation of the process of luminescence quenching in dioxane–water solutions excited with γ radiation. It was therefore considered worthwhile to investigate further the effect of water on the components of the solution (1,4-dioxane and the luminescent admixture) and to explain the mechanism of excitation energy quenching for both components of the solutions separately. For comparison, the

inefficient solvent methanol was used as the diluent for 1,4-dioxane instead of water.

2. Experimental details

To prepare the scintillating solutions, spectroscopically pure 1,4-dioxane and methanol were used together with triply distilled water and 2,5-diphenyloxazole (PPO) from Nuclear Enterprises, Edinburgh, Gt. Britain (scintillation grade; used without additional purification). Oxygen was not removed from the solutions. The luminophore concentration was fixed while the concentration of the second solvent X_2 in dioxane was varied from 0 vol.% to about 40 vol.%. The relative radioluminescence yield and scintillation decay time were measured using the instruments described in ref. 3. For the excitation of the solution γ radiation from cobalt-60 was used. The photoluminescence investigations consisted of measuring the yield, spectra and luminescence decay time for the acceptor PPO alone on direct excitation by radiation of wavelength 313 nm.

3. Discussion of results

It is difficult to investigate dioxane as a donor directly because its spectra lie within the vacuum UV region [5]. For this reason, the PPO admixture was used as an "internal detector" providing information on the quenching processes in 1,4-dioxane.

From the results of the measurements, shown in Figs. 1 and 2, it is evident that the radioluminescence quenching I_0/I and reduction in the scintillation decay time $(\tau_0/\tau)_s$ are proportional to the concentration $[X_2]$ of the second solvent (water or methanol). This made possible the calculation,
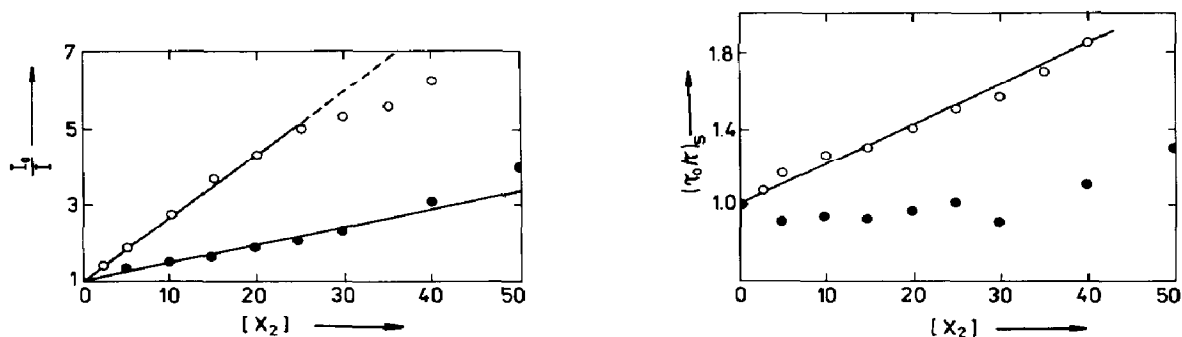

Fig. 1. Relative radioluminescence efficiency I_0/I of dioxane PPO solutions plotted against $[X_2]$ (vol.%) of the second solvent (fixed PPO concentration of 10 g l^{-1}): ○, water; ●, methanol.

Fig. 2. Scintillation decay times $(\tau_0/\tau)_s$ vs. $[X_2]$ (vol.%) of the second solvent (PPO concentration, 10 g l^{-1}): ○, water; ●, methanol.

based on the Stern–Volmer relation

$$\frac{I_0}{I} = 1 + \sigma[X_2]$$ (1)

and

$$\left(\frac{\tau_0}{\tau}\right)_s = 1 + \sigma^\tau[X_2]$$ (2)

of the Stern–Volmer quenching constants σ and σ^τ (Table 1) as well as the half-value concentrations $[X_2]_h$ (for which $I = (1/2)I_0$ and $\tau = (1/2)\tau_0$).

It follows that (1) the radioluminescence of 1,4-dioxane solutions is quenched by water more efficiently than by methanol ($\sigma_{meth} < \sigma_{water}$), (2) for water $\sigma > \sigma^\tau$ and (3) for methanol $\sigma^\tau = 0$.

TABLE 1

Radioluminescence quenching parameters of investigated solutions

Solution	σ^τ (l g^{-1})	$[X_2]_h^\tau$ (g l^{-1})	σ (l g^{-1})	$[X_2]_h$ (g l^{-1})	σ_{corr} (l g^{-1})	$[X_2]_h^{corr}$ (g l^{-1})
Dioxane–water–PPO	0.002	500	0.016	62	0.011	90
Dioxane–methanol–PPO	0	—	0.006	166	0.003	310

Photoluminescence measurements have shown that the presence of water has the following effects: (a) a slight reduction in the quantum yield for PPO (Fig. 3); (b) an increase in the luminescence decay times (Fig. 4); (c) an alteration of the luminescence spectra (Fig. 5), with absorption spectra remaining unchanged; (d) an increase in the photoluminescence decay times, measured in the luminescence band, with increasing wavelength (Table 2).

These observed properties of photoluminescence of PPO are characteristic of excimers [6]. Thus it can be assumed that water stimulates the excimer formation of PPO. But the influence of water on PPO does not explain the behaviour of the radioluminescence efficiency and the scintillation decay time. The strong reduction in radioluminescence intensity suggests that the quenching process in the solvent 1,4-dioxane must be responsible for it.
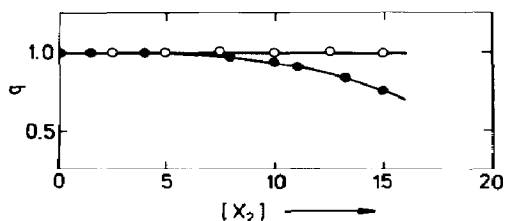

Fig. 3. PPO quantum yield q vs. $[X_2]$ (vol.%) of the second solvent (PPO concentration, 10 g l^{-1}): ●, water; ○, methanol.
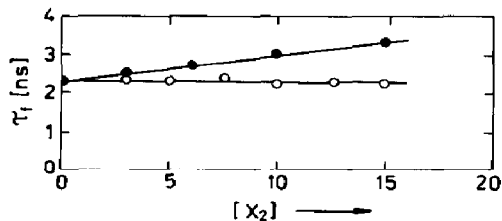
Fig. 4. Photoluminescence decay times τ_f plotted against $[X_2]$ (vol.%) of the second solvent (PPO concentration, 10 g l^{-1}): ●, water; ○, methanol.
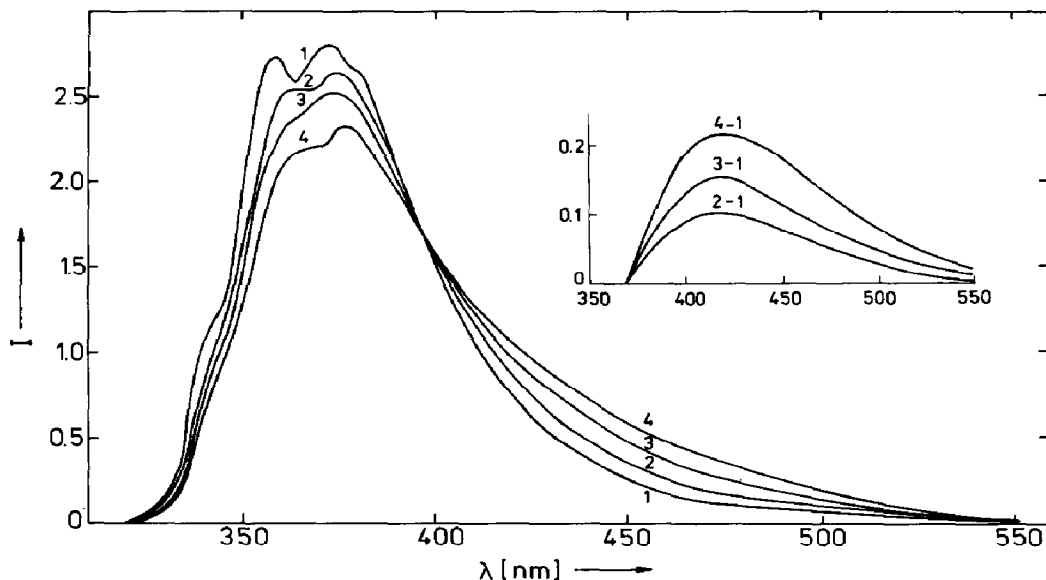
Fig. 5. Luminescence spectra for PPO in dioxane (water concentrations: curve 1, 0 vol.%; curve 2, 20 vol.%; curve 3, 30 vol.%; curve 4, 40 vol.%; curves 2-1, 3-1 and 4-1, excimer spectra for water concentrations of 20 vol.%, 30 vol.% and 40 vol.%).

TABLE 2

Photoluminescence decay times of PPO measured at various wavelengths in the luminescence band

λ_{obs} (nm)	350	375	400	425
τ_f (ns)	1.5	2.6	2.8	3.5

Associates of 1,4-dioxane–water having a lower quantum yield than uncomplexed 1,4-dioxane molecules [5] may cause the decrease in the radioluminescence intensity.

That $\sigma^\tau < \sigma$ for the 1,4-dioxane–water solution of PPO may be explained by the presence of complexes of the components of the solution. The shortening of the lifetime of the PPO molecular luminescence by water is partially compensated by the longer decay time of the excimer luminescence (Table 2), whose intensity increases with an increase in the water concentration.

The resultant effect of these processes should give at least a bi-exponential decay time. Since our counter [3] only allows us to measure a mean scintillation decay time τ_s, the shortening of τ_s should be treated merely as an indication of the complication of the radioluminescence process. Therefore the Stern–Volmer formulae (1) and (2) are not equivalent in this case ($\sigma^\tau \neq \sigma$) and it is formula (1) that gives the correct values for the quenching constant.

It is worth noting that the radioluminescence intensity of liquid solutions (for the acceptor concentrations used in this work) depends mainly on

non-radiative electron excitation energy transfer over long distances and does not depend on the viscosity [7]. This means that the diffusion process does not influence the radioluminescence intensity. So it can be expected that a change in temperature of the solution should reveal the influence of the associates on the radioluminescence process.

From the analysis of the results presented in Fig. 6, based on the Arrhenius equation $\ln(I/I_0) = -\Delta E/kT$, one energy of activation $\Delta E_1' = (0.09 \pm 0.005)$ eV was obtained for the 1,4-dioxane–PPO solution (not containing water), while for the dioxane–water–PPO solution two energies of activation, $\Delta E_1 = (0.06 \pm 0.005)$ eV and $\Delta E_2 = (0.02 \pm 0.005)$ eV, were obtained. The activation energy $\Delta E_2 = 0.02$ eV is supposedly the energy of bonding of dioxane–water associates. A similar value of the bonding energy of 1,4-dioxane–water complexes has been found using a different method [8]. The presence of these associates (in which the ratio of 1,4-dioxane to water molecules is 2:1), characterized by the lower efficiency of the excitation energy transfer [4] compared with unassociated dioxane molecules, provides a satisfactory qualitative explanation of the diagram shown in Fig. 6.
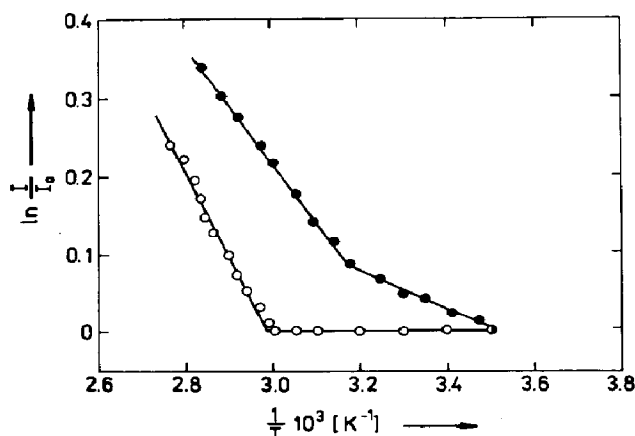

Fig. 6. Relative radioluminescence efficiency *vs.* temperature (PPO concentration, 10 g l⁻¹): ●, dioxane–water solution, water concentration equal to 7.5 vol.%; ○, solution without water.

The activation energies $\Delta E_1'$ and ΔE_1 are the energies of bonding of PPO excimers in pure dioxane and in the dioxane–water solution respectively. Differences in the bonding energy of PPO excimers in these two different media might be explained by differences in their dielectric constants [9] ($\epsilon \approx 2$ for dioxane; $\epsilon \approx 5.2$ for a mixture of dioxane with 7.5 vol.% water).

Using methanol for the dilution of 1,4-dioxane does not affect the spectra, quantum yield and PPO luminescence decay times. The scintillation decay times also remain constant. It should be assumed, based on the constancy of $(\tau_0/\tau)_s$ for PPO solutions in 1,4-dioxane–methanol, that radioluminescence is not quenched by methanol. The decrease in the relative radioluminescence efficiency observed in the experiments occurs because of the substitution of the molecules of the efficient donor dioxane by the inefficient

methanol or water molecules, which (it is assumed) do not transfer the excitation energy to the acceptor. Taking into account this effect one can obtain a corrected value for σ [10]:

$$\sigma_{corr} = \left\{\frac{I_0}{I}(1 - [X_2]) - 1\right\}[X_2]^{-1} \tag{3}$$

where $[X_2]$ denotes the mole fraction of the inactive solvent. Table 1 shows the values of σ_{corr} together with the corresponding half-concentrations. It follows that the quenching effect of methanol, however weak, is distinct and may be caused by quenching of excited dioxane molecules by short-lived products of methanol radiolysis [11].

4. Conclusions

The quenching effect of water with respect to radioluminescence of 1,4-dioxane solutions of PPO consists of quenching of directly excited 1,4-dioxane molecules as well as acceptor–PPO molecules excited indirectly (by the transfer of excitation energy). The quenching takes place both because of the formation of 1,4-dioxane–water associates (bonding energy $\Delta E = 0.02$ eV) and the increase in PPO excimerization in the presence of water. According to the results, the energy of bonding of PPO excimers may depend on the dielectric constant of the medium.

Excitation of solutions with γ radiation leads to radiolysis products which cause the quenching of the donor excitation energy. This probably occurs in very short times compared with the time of scintillation decay.

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