INVESTIGATION OF THE MECHANISM OF RADIOLUMINES-CENCE IN DIOXANE SCINTILLATORS

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A study has been made of the dependence of radioluminescence efficiency and decay times of the scintillations of dioxane solutions of PPO and the quenching influence of water upon radioluminescence efficiency and decay times of the scintillations at fixed concentrations of the solute.

The quenching constant of radioluminescence by water σ equals 12.6 ml/ml and the quenching constant computed from the change of decay time σ^τ equals 3.44 ml/ml. This allows one to assume that the "quenching" activity of water is conditioned by the appearance of solvational coats around the molecules of the solute which reduce the probability of excitation energy transfer to the molecules of PPO by collisions.

1. Introduction

Although dioxane belongs to effective solvents in the Furst-Kallmann classification [1], so far few investigations of it have been carried out on account of its small radioluminescence efficiency as compared with such solvents as: xylene, toluene, and benzene. One of the features which increases the detecting capacities of dioxane scintillators is the fact that they go into solution with water very readily. This makes it possible to apply dioxane-water solutions of various solutes to the detection of low energy β-radiation emitted by ^3H or ^{14}C, introduced with water or water solutions containing these isotopes [2–7].

As shown in papers [2–5] water causes a decrease of radioluminescence efficiency of dioxane solutions. This so-called quenching activity of water may appear at various stages of the process of radioluminescence.

a) Water molecules absorb the energy of exciting nuclear radiation without any influence upon the luminescence and excitation energy transfer to the solute. On account

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of this, the relative radioluminescence efficiency should decrease with the increase of water concentration. The decay time of scintillation should remain constant.

b) Water may cause a deactivation of the excited dioxane molecules. The decrease of luminescence efficiency should be greater than in case a) and should be determined by the law of quenching by foreign substances [8, 9].

c) The water introduced into the solvent may decrease the quantum yield of luminescence of the acceptor.

Upon direct excitation of the acceptor its photoluminescence efficiency should change with the concentration of water.

d) Water may decrease the efficiency of excitation energy transfer from dioxane to the solute. It should be borne in mind that a very weak absorption band of dioxane in the range of waves < 230 nm, and a low quantum yield of its luminescence, [10], do not create favourable conditions for energy transfer [7, 9]. In spite of that, dioxane is a good solvent [1] and efficiently transfers excitation energy to the solute.

For that reason, the variation mechanism of excitation energy transfer from dioxane to solutes on changing concentration of the latter is also interesting.

An investigation of the aspects of radioluminescence in dioxane solutions outlined above is the subject of the present work.

2. Experiments

To prepare the solutions we have used dioxane *p. a.* (made by XENON — Łódź), 2,5-diphenyloxazole (PPO) of scintillating degree of purity (made by Nuclear Enterprises Edinburgh) and threefold distilled water. Measurements of relative radioluminescence efficiency (I_γ), of decay time of scintillation (τ), relative quantum yield of fotoluminescence (I_f), and emission spectrum, have been carried out on these solutions. For measurements made at a temperature of $20 \pm 1°C$ we have used the apparatus described in reference [11]. The solutions were excited by γ-radiation (^{60}Co). The results are presented in Figs 1–4.

3. Discussion of the results

The dependence of I_γ on the concentration of PPO (Fig. 1) has a similar character as in other scintillating solutions [7]. It results from the increase of efficiency of excitation energy transfer from a solvent to a solute upon increasing concentration of the solute [12]. The dependence I_γ is typical for the case when the solvent is a highly efficient donor. For "poor" solvents *e. g.* ethyl alcohol I_γ increases very slightly with the concentration of the solute [13]. The decay time scintillation also becomes longer with the increase of the concentration of the acceptor as in other systems described in papers [14–16], when excitation energy transfer from the solvent to the dissolved solute occurs. The results of the measurements presented prove that in the tested solutions electronic excitation energy transfer occurs from dioxane molecules to the molecules of PPO when the solution is excited by γ-radiation.
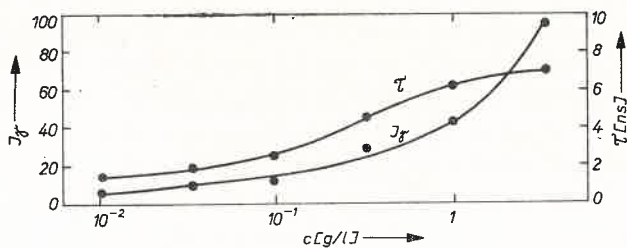
Fig. 1. Dependence of relative radioluminescence efficiency (I_γ) and decay time of scintillation (τ) on the concentration (c) of PPO in dioxane
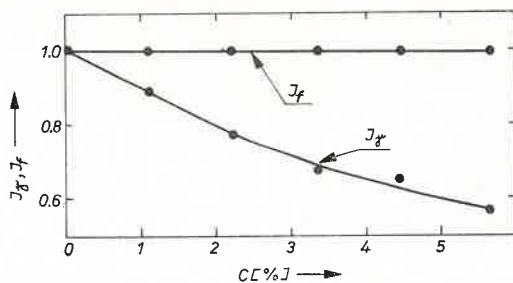

Fig. 2. Dependence of relative quantum yield of photoluminescence (I_f) and relative radioluminescence efficiency (I_γ) on water concentration (c) in dioxane solutions of PPO. I_f — excitation by light of a wavelength $\lambda = 313$ nm. The concentration of PPO (3.33 g/l) is constant for all the solutions
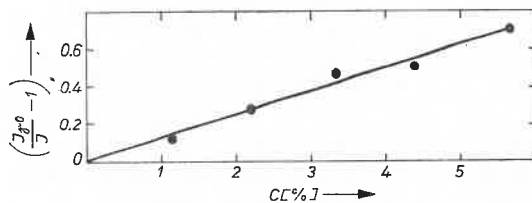

Fig. 3. Relative radioluminescence efficiency $\left(\dfrac{I_{\gamma 0}}{I_\gamma} - 1 \right)$ as a function of water concentration in dioxane solutions of PPO. The concentration of PPO (3.33 g/l) is constant
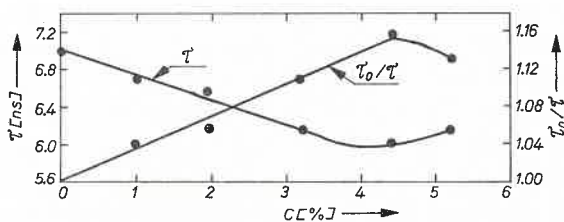

Fig. 4. Dependence of decay time of scintillation (τ) on water concentration (c) in dioxane solutions of PPO. The concentration of PPO (3.33 g/l) is constant

Certain pieces of information about the mechanism of energy migration can be obtained by testing the influence of water on the process of radioluminescence.

In Fig. 2, the dependence of radioluminescence efficiency of a dioxane solution of PPO on concentration of water exhibits a great change in the tested range of water concentrations. The quantum yield of photoluminescence of the same solutions excited by light of wavelenth $\lambda = 313$ nm is constant. In this case light directly excites the molecules of PPO. The constancy of quantum yield of PPO proves the decay time of luminescence of the PPO molecules will also be constant, independently of water concentration. Emission spectra of PPO do not change under the influence of water, either.

The linear dependence $I_{\gamma 0}/I_{\gamma}$ (presented in Fig. 3) leads to the conclusion that quenching of dioxane — PPO solutions by water is subject to the Stern-Volmer law

$$\frac{I_{\gamma 0}}{I_{\gamma}} - 1 = \sigma c \tag{1}$$

where $I_{\gamma 0}/I_{\gamma}$ denote intensities of radioluminescence of an anhydrous solution and of one with an admixture of water, c — water concentration, σ — quenching constant, the inversion of which denotes half-concentration ($c_{1/2}$) such that $I_{\gamma} = 1/2 \cdot I_{\gamma 0}$. Computed from expression (1), the quenching constant of a dioxane-PPO solution, σ, equals $12.5 \frac{ml}{ml}$ and, corresponding to it, the half-concentration, $c_{1/2}$, equals $0.079 \frac{ml}{ml}$. The decay time of scintillation of the solutions discussed, presented in Fig. 4, is subject to the Stern-Volmer law, expressed by

$$\frac{\tau_0}{\tau} - 1 = \sigma^{\tau} c. \tag{2}$$

Here τ_0 and τ denote the decay time of the scintillation of an anhydrous solution and with an admixture of water of concentration c, respectively.

Computed in this way, $\sigma^{\tau} = 3.34 \frac{ml}{ml}$ ($c_{1/2} = 0.29$) is much smaller than σ.

The measured dependences prove that in the process of radioluminescence of dioxane-PPO solutions, there appears a remarkable quenching while the decay times of scintillation are slightly shorter. On the other hand, however, the quenching constant of radioluminescence of dioxane without solutes is limited only to nonactive absorption of excitation energy [5]. Thus on the basis of the results presented in Figs 2 and 3 we should conclude that water inhibits excitation energy transfer from the donor (dioxane) to the acceptor (PPO).

Consequently the excitation energy of dioxane molecules undergoes inner reduction; the radioluminescence efficiency decreases. The significant role of water in causing a great decrease of the radioluminescence of dioxane-PPO solutions can be explained by the appearance of a solvational coat around the molecules of PPO [18, 19]. The dipole moment

of PPO, μ, equals 2.73 D [20] and the dipole moment of water molecules, μ_{H_2O}, equals 1.87 D, so we can assume that electrostatic coupling will cause such an effect.

Solvational coats may protect the molecules of PPO from a collision with the excited molecules of dioxane making excitation energy transfer at direct contact impossible. Thus we should assume that excitation energy transfer is brought about by collisions. A slower decrease of decay time of scintillation upon increase of water concentration as compared with I_γ points out that the process of radioluminescent quenching of solutions by water goes very fast.

It seems probable that in the case of solution excitation by γ-radiation — when excitation to all the states is effected — a partial deactivation of higher excitation states of dioxane by water molecules is possible, particularly at higher concentrations of water. That would explain in this case, why the value of σ for dioxane-water solutions is somewhat higher than 1. Water molecules could then play the role of a nonluminescent acceptor of energy competing with the molecules of PPO in the deactivation of dioxane molecules. Such an activity of $CHCl_3$ molecules with regard to higher excited states of other "good" solvents has been reported by Levin and co-workers [21].

For dioxane solutions it is difficult to prove the rightness of this assumption due to a very small value of the absorption coefficient of dioxane in the far ultraviolet range.

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