

Mechanism of radioluminescence of condensed organic media

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A description is proposed for the mechanism of formation of the fast component of the radioluminescence pulse in organic molecular media. The description takes into account the specific nature of the change in the energy of charge states in objects which are in different aggregate states. In contrast with the existing theory of radioluminescence, which ignores the specific nature of the process leading to a change in the charge states, this description makes it possible to overcome the crisis that arose in the theory at the end of the 1970s, after precise measurements of the leading edge of the radioluminescence pulse of vinyl aromatic plastics were carried out.

With respect to structural complexity, organic substances used in scintillation technology [organic single crystals (OS), plastic scintillators (PS), and liquid scintillators (LS)] fall within a wide intermediate region between inorganic crystals and molecular biosystems. In the investigation of radioluminescence this circumstance makes it possible not only to study the characteristic features of this process but also to develop on the basis of such systems, just as on model systems, procedures, and methods for studying more complicated structures.

The theory of radioluminescence developed for organic condensed media by Birks,¹ Voltz,² and a number of other authors (see the review article by Brooks³ regarding this point) ignored the effect of the change in charge states on the formation of the radioluminescence pulse. The shape of the light pulse (excluding its slow components⁴) should then have the same analytical description for radio- and photo-excitation, and the leading edge of the radioluminescence pulse for an organic solid should have an initial section of rapid growth, followed by a decrease in the pulse slope. For liquids the shape of the fast component of the pulse should be described by the expression

$$i(t) \sim \exp(t/\tau_1) * \exp(t/\tau) \equiv \int_0^t \exp(-(t-\theta)/\tau_1) \exp(-\theta/\tau) d\theta, \quad (1)$$

where * indicates a convolution, t is the elapsed time after the excitation, and τ_1 and τ are the pulse rise and decay times.

The first investigations of the shape of the leading edge for PS,^{5–8} performed on an apparatus with subnanosecond time resolution, gave results opposite to the theoretical predictions.¹ A slow section was followed by an increase in the slope of the radioluminescence pulse. The pulse was described by the expression

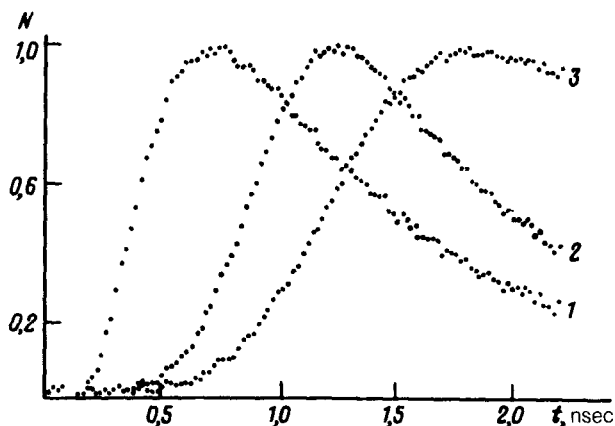


FIG. 1. Radioluminescence kinetic curves for two-component liquid scintillators (curve 1), plastic scintillators (curve 2), and organic single crystals (curve 3).

$$i(t) \sim f_G(t) * \exp(-t/\tau), \quad (2)$$

where

$$f_G(t) \sim \exp(-(t-3\sigma)^2/2\sigma^2), \quad (3)$$

σ is a constant with the dimension of time, and the remaining notation is the same as Eq. (1). A similar effect was also observed for OS, and the effect of the controllable change in their structural perfection (achieved by using special growth methods⁹), which affected the concentration of deep charge-carrier and exciton trapping centers, on σ (3) was extremely small.¹⁰ For liquid scintillators the pulse shape was described by expression¹¹ (1). The situation is illustrated in Figs. 1 and 2 for the example of LS [0.034 moles/liter 2-phenyl-5(4-biphenyl)-1,3,4-oxadiazole (PBD) in toluene], PS (3.46% PBD in polyvinylxylo), and OM (0.042% diphenylbutadiene in *p*-terphenyl). For the kinetics described by curve 3 (Fig. 2), the moments of excitation of the macromolecules of the base and therefore also the molecules of the luminescent additive are characteristically delayed with respect to the situation described by curve 2. The emission time τ for these LS and PS are virtually identical (0.94 nsec and 0.90 nsec), and for this reason the delay $\sim 10^{-10}$ sec observed for curve 2 (Fig. 1) with respect to curve 1 can be caused only by processes preceding transfer of electronic excitation energy to the molecules of the luminescent additive. The existing theory cannot explain these results.^{6,8} We shall analyze the situation in order to clarify the discrepancies between the theory¹ and experiments.

The values of σ (Refs. 5-9) obtained for different objects were $\sim 10^{-10}$ sec. These values are markedly higher than the computed electronic excitation energy transfer times ($\leq 10^{11}$ sec) for them.^{7,8} It is quite logical to assume that the additional delay, described by expression (3), of the emission of radioluminescence photons is due to the localization of charge carriers at shallow structural trapping centers. This localization precedes recombination of the carriers, which in turn engenders excited states

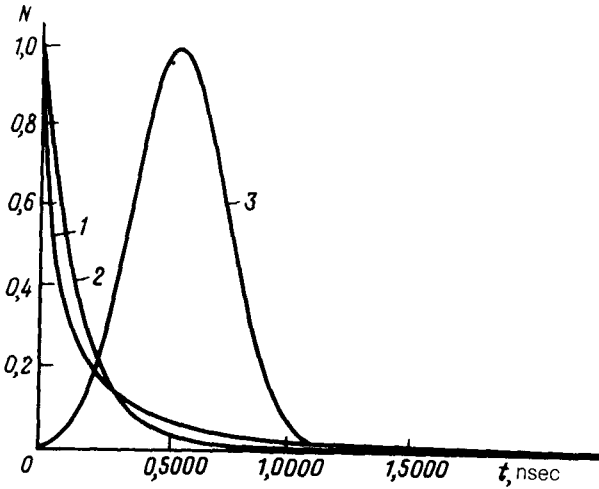


FIG. 2. Excitation probability density for molecules of a luminescent additive in the process of their quenching of excitation of the base molecules for liquid scintillators (curve 1) and plastic scintillators (curve 2—calculated according to Ref. 1; curve 3—according to experimental data).

and precedes luminescence. According to Eq. (3), the most likely localization time of charge carriers is $\tau_l = 3\sigma$. The corresponding depth of the trapping center will then be

$$E_t = kT \ln(\tau_l \nu), \quad (4)$$

where k is Boltzmann's constant, T is the temperature, and ν is the frequency factor. Since the experiments⁵⁻¹¹ were performed at room temperature, for OS and PS we have¹⁰ $E_t \leq 0.17$ eV. Trapping centers with these values of E_t (Fig. 3, curve 1) can be associated with low- and medium-angle boundaries of the OS lattices or spatial non-

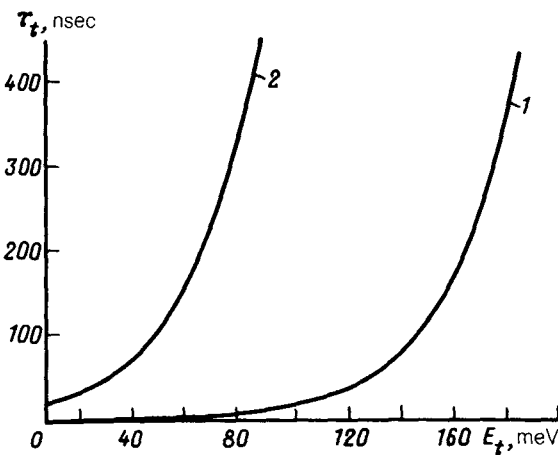


FIG. 3. Computed curve of τ_t versus E_t (4) neglecting (curve 1) and allowing for (curve 2) the polarization effect.

uniformities of PS macromolecules.^{10,11} However, what explains the small difference in the values of σ for different OS and PS? The answer to this question can be based on the following argument. In solid-state organic molecular systems, a charge carrier, having fallen into a trapping center, polarizes the OS molecules (or fragments of macromolecules of the PS) surrounding it. The result of the interaction of the charge with the dipoles induced on neighboring molecules can be represented as a deepening of the trapping center by an amount δE_t . This deepening is virtually the same for a wide class of organic compounds employed in scintillation technology for growing OS and its characteristic value is¹² $\delta E_t \sim 0.1$ eV. The estimated depth of the initial structural trapping center (Fig. 3, curve 2) is $E_t - \delta E_t \leq 0.07$ eV or ~ 2 kT at room temperature. The existence of very shallow charge-carrier trapping centers, most of which can be produced by temperature-activated vibrations of the OS lattice or fragments of PS macromolecules, thus completely explains the appearance of the additional delay, described by the expression (3), of the emission of the radioluminescence photons, while the theory of radioluminescence must take into account the formation of molecular polarons in organic solids as a result of excitation of the polarons by ionizing radiation. The last assertion explains the experimentally observed correspondence between the description (1) and the shape of the scintillation pulse for LS, where, as can easily be shown, because of efficient diffusion processes, the appearance of a stable polarization environment around an ion is possible only at distances (Refs. 10 and 11) < 10 Å, i.e., comparable to the size of the molecule. Therefore, the duration of the recombination process is determined by the characteristic collision frequency of the molecules¹⁰ ($\sim 10^{12}$ sec⁻¹). It also points to a new application of the results obtained in investigations of radioluminescence of organic solids. By studying their emission kinetics it is possible to investigate polarization-origin trapping centers which are formed as a result of the formation of charge carriers in a material after the material is excited by ionizing radiation.

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