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Organic Scintillators

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Organic Scintillators

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Internal Conversion and Scintillation Efficiencies

S. LIPSKY

The total fluorescence efficiency of pure liquid benzene for excitation at 2537 Å is 0.032 with approximately equal contributions from monomer and excimer configurations. At 1200 Å, the total fluorescence efficiency is reduced by *c*. 0.6 but with little change in the spectral distribution. At intermediate wavelengths, as has previously been reported, the fluorescence efficiency is approximately anticoincident with the absorption coefficient exhibiting a minimum of 1880 Å *c*. 0.35 times the long wavelength yield.

For optical excitations in the first band there seems to be a high efficiency for intersystem crossing to the triplet state. For shorter wavelength excitation, intersystem crossing with ultimate production of the lowest triplet does not appear to be the process that is responsible for the decrease in fluorescence efficiency. Recent studies of the vapor phase photolysis of benzene at 1849 Å indicate a disappearance quantum yield of 0.25 at 1 torr with extrapolation to 1.0 at zero pressure. It has been suggested that the observed disappearance results predominantly from a predissociation out of the ground electronic state, implying thereby a high level of photochemical stability in the liquid.

The results of the above studies are discussed in connection with a recent determination of the scintillation efficiency of benzene and p-terphenyl for $C^{14}\beta$ excitation in the limit of unit transfer efficiency of 0.012. This corresponds to a G value for production of $^1B_{2u}$ benzene of 1.6.

On The Vacuum Ultraviolet Excited Luminescence of Pure and Doped Polystyrene

A. WEINREB and M. LEIBOWITZ

The overall fluorescence yield and fluorescence spectrum of polystyrene as well as the fluorescence yield of solid solutions of anthracene and of diphenyloxazole in polystyrene are studied as a function of excitation wavelength in the region 584–3000 Å. In all cases a strong dependence of the investigated properties on excitation wavelength is found.

The fluorescence yield and spectrum of polystyrene in solution is basically different from that of the solid phase. For the fluorescence yield of the solid two basic types of behavior are found, depending on the preparation and treatment of the sample. The remarkable dependence of the fluorescent spectrum of solid polystyrene on excitation wavelength is also strongly depending on the mode of preparation. In all cases there is a pronounced correlation between the absorption spectrum of polystyrene and its fluorescent properties, a greater intensity and stronger red shift corresponding to a higher absorption coefficient.

The variation in fluorescence yield of plastic solutions of anthracene and diphenyloxazole in polystyrene with excitation wavelength is very different from that for pure polystyrene. In fact for highest acceptor concentrations the former is practically opposite to the latter, indicating a strong competition between exciton transfer within the solvent and transfer to the solute.

Some remarkable coincidences between luminescent behavior and double refraction are observed.

The results indicate the decisive influence of the state of aggregation as well as the structure of the solid on the luminescent behavior for excitation of higher electronic levels.

The Effect of Solvent Dilution on Solvent–Solvent Energy Migration in Liquid Scintillator Materials

J. T. DUBOIS and J. VAN LOBEN SELS

Previous work by the authors† has established the magnitude of solvent–solvent electronic energy migration in the neat (undiluted) scintillator solvents benzene, toluene and *p*-xylene. Using a similar technique, the effect of progressive dilution of the neat solvents by n-hexane and by cyclohexane has been investigated. The new results show that solvent–solvent migration is a linear function of donor concentration, independent of the diluent, and they shed light on the apparently conflicting reports of other workers.

Measurement of Transfer Efficiencies and Radiative Transfer in Aromatic Solvents at Very Low Solute Concentrations‡

D. L. HORROCKS

The relative light yield was measured over a range of solute concentrations in an aromatic solvent for excitation with electrons and alpha particles. The resultant curve is described by an equation which relates to the possible processes occurring in the scintillator solution; solvent emission, solvent transfer, solvent self-quenching, external solvent quenching, specific ionization track quenching, solute emission, solute self-quenching, external solute quenching and a radiative energy transfer which occurs at very low solute concentrations.

The relative light yields were measured for PPO in toluene over the concentration range of 10 g/l. to 10 mg/l. and for dimethyl POPOP in toluene over the concentration range of 2 g/l. to 5 mg/l. The radiative solvent–solute energy transfer will be discussed. Also other interesting results obtained from the final equation will be presented.

† Munich Symposium, September 1965.

‡ Work performed under the auspices of the U.S. Atomic Energy Commission.

Fluorescence Quenching and External Spin-Orbit Coupling Effects

A. KEARVELL and F. WILKINSON

The quenching of the fluorescence of anthracene and several of its meso-derivatives by "heavy atom quenchers" in various solvents has been shown to be dependent on the solvent, the quencher, and especially on the nature of the substituent. Anthracene shows good agreement with the Stern–Volmer equation in all solvents even in the presence of very high concentrations of quencher. However, marked deviations from this equation are observed for many anthracene derivatives and in some cases the heavy atom "quencher" leads to an increase rather than to a decrease in the fluorescence.

Possible reasons for this behaviour are discussed and bimolecular rate constants for quenching are given where appropriate.

Energy Transfer and Quenching in Plastic Scintillators

F. HIRAYAMA, L. J. BASILE and C. KIKUCHI

Effects of added chloro- and bromo-substituted organic compounds on luminescence properties of plastic scintillators have been investigated. The plastic systems studied were polystyrene + 9,10-diphenylanthracene + quencher and polystyrene + quencher. For the latter system, the residual styrene monomer left in the samples was regarded as a fluorescent solute, since the fluorescence of bulk thermally polymerized polystyrene is entirely that emitted from the residual monomer, not from polystyrene itself. The quenchers used were: *p*-dichlorobenzene, *p*-dibromobenzene, hexachlorobenzene, 1,2,3,4,5,6-hexachlorocyclohexane, 2-chloronaphthalene and 2-bromonaphthalene. For these samples, the light output under UV and beta-ray excitation, and the fluorescence decay time under pulsed electron excitation were measured.

Experimental data were analyzed by typical quenching kinetics. By such analyses, the solvent and solute quenching constants α and β, which characterize the ability of the quencher to quench the excited plastic solvent and fluorescent solute, respectively, were determined for each sample series. On the other hand, under the assumption that solvent and solute quenching are due to energy transfer from the excited solvent and the excited solute, respectively, to the quencher, theoretical values of α and β were calculated from the optical data of individual components of the samples, making use of Förster's theory of electric dipole–dipole energy transfer.

In calculating the solvent quenching constant α, excimer formation in a polystyrene molecule has been taken into account: the fluorescence spectrum of pure polystyrene (free from the residual monomer) in solid phase and in liquid solution shows that an excited phenyl segment of polystyrene efficiently forms an eximer (a transient dimer) with an unexcited segment. Calculation of α was thus made for two extreme cases: "Case S"—energy transfer is assumed to occur directly from the excited segment of polystyrene to the fluorescent solute or to the quencher before excimer formation takes place; "Case D"—energy transfer is assumed to occur from the excimer after it has been formed.

Experimental values of α for UV excitation are found to compare much more favorably with the values calculated for Case S than those calculated for Case D, supporting the Case S transfer by dipole–dipole interaction as a means of energy transfer. This finding is further interpreted as an indication of the occurrence of efficient energy migration through the polystyrene medium.

Luminescence quenching under beta-ray excitation was generally greater than that under UV excitation. In particular, in sample series containing hexachlorocyclohexane, no quenching was observed under UV excitation, while under beta-ray excitation the decrease in luminescence output was as large as 50 % at the maximum quencher concentration. It is suggested that this phenomenon may result from the occurrence of energy transfer at higher excited states of polystyrene.

Observed solute quenching in some series of polystyrene + 9,10-diphenylanthracene + quencher is not accounted for by usual mechanisms of quenching. Such quenching can be explained by assuming the energy transfer from the singlet excited state of 9,10-diphenylanthracene to the triplet state of the quencher.

The Validity of Perrin's Equation in Solute Quenching

C. T. PENG

The striking similarity between the radioactivity-concentration quenching curve of a ^{14}C-, ^{35}S- or ^{3}H-labeled quencher in a liquid scintillation system[1, 2] and the fluorescence intensity-concentration quenching curve of a solvent–solute system[3] is noteworthy. The former can be replotted to yield a linear relationship between the apparent specific radioactivity and an exponential function of the quencher concentration.[2] The use of this exponential factor in quenching correction is justifiable from a mechanistic point of view because such a factor is resulted from an approximation of Förster's resonance transfer mechanism[4] with the assumption that within the critical transfer distance, an instantaneous transfer of the excitation energy takes place but no transfer beyond that distance, and also from a probable mechanism of excitation transfer between the triplet states of the molecules in solution, analogous to that between the donor and the acceptor in a sensitized luminescence system.[5, 6] A similar exponential form was proposed by Perrin[7] for expressing the self-quenching of fluorescence of a solute.

The validity of Perrin's equation $\phi = \phi_0 \exp(-c/c_m)$ as given, where ϕ is the fluorescence power which tends to ϕ_0 as the concentration, c, tends to zero, and c_m, the concentration for maximum fluorescence, is disputed by others.[8, 9] If ϕ is redefined as apparent specific fluorescence intensity, namely, the observed intensity per unit concentration of solute and ϕ_0 as the specific fluorescence intensity in the absence of self-quenching, then Perrin's equation becomes generally valid in a qualitative sense. The fluorescence intensity-concentration quenching curves of Furst and Kallmann[3] on organic scintillators in solution, described by the equation $I = Pc/(Q+c)\ (P+c)$, where I is the intensity, c, the solute concentration, and P, R, and Q are constants, can be replotted using log (I/c) versus c to afford curves from which "relative" critical transfer concentrations and "relative" specific fluorescence intensity or power of the solute can be obtained. A few of the related samples were found to yield parallel curves which were not apparent from the assigned P, R, and Q values. In many cases, the reported P/R values were also obtained by extrapolation to zero solute concentration.

The validity of the redefined Perrin's equation were further verified using tritium-labeled organic scintillators, such as 1,2-benzanthracene, carbazole, 2,5-diphenyloxazole, 1,4-bis-2-(4-methyl-5-phenyloxazolyl) benzene, naphthalene, *alpha*-naphtylphenyloxazole, *p*-terphenyl, etc. The magnitude of the observed radioactivity in association with the quenching curves of these labeled scintillators in solution increases with increasing solute concentration and is greater by a factor of c than that of the corresponding nonlabeled scintillator containing a given source of the same label. Similar phenomenon has been observed with labeled quenchers.[1]

The shape of the quenching curve of the solvent–solute systems measured with a liquid scintillation spectrometer, showed variations with instrument sensitivity and source of irradiation (^{226}Ra, ^{14}C or ^{3}H). The presence of a quencher and the use of an inefficient solvent also affect the shape of the curve, chiefly by diminishing the fluorescence intensity at low solute concentrations. Since the quenching curve reflects the energy transfer process in solution, thus from such changes a comparison can be made of the efficiency in excitation transfer, self-quenching, and specific fluorescence intensity of organic scintillators in solution.

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The Luminescence Decay of Organic Scintillators

G. LAUSTRIAT and A. COCHE

Results obtained in the laboratory on the decay of the scintillation in organic materials are reviewed.

We first consider the processes leading to molecular excited singlet states S_1, some of these being directly generated (after internal conversion from upper excited states S_n) by the charged particles and giving rise to a fast emission whose decay is the same as the fluorescence of the medium ("prompt signal"), the others resulting from interaction between two triplet states T_1 and being responsible for the slow emission ("delayed signal").

From the kinetics of the processes involved in these two signals, it is possible to give an accurate interpretation of the decay curves of the scintillation in single crystals (anthracene and stilbene) and in solutions. In this latter case, the oxygen effect on the slow component is shown to be due to the quenching of the triplet states.

For different ionizing radiations, the delayed signal has the same decay law, but its intensity depends on the nature (charge and specific energy loss) of the incoming particles. A technique using this well-known property and, allowing a discrimination between electrons, protons and α-rays, is presented.

Fluorescence Decay of Liquid Scintillator Systems

P. K. LUDWIG

When liquid scintillator systems are excited by short pulses of high energy radiation it is commonly observed that the resulting fluorescence does not follow a simple exponential decay law. In order to obtain a better understanding of the processes involved in the deactivation of the excited states, fluorescence decay measurements were carried out as a function of temperature and scintillator concentration.

Typical systems like toluene/PPO-, cyclohexane/PPO-solutions were excited by 30 kV X-ray pulses of up to 25 nsec duration and the resulting fluorescence decay followed by a modified optical sampling technique (Dresskamp-Burton) over a wide range of temperatures. For comparison corresponding experiments were performed using short UV-pulses for excitation and a monophoton-technique for following the fluorescence decay.

The fluorescence decay of these systems is characterized by an initially rapid decay which gradually becomes slower with the slower part more pronounced at lower temperature. A preliminary analysis of the spectral composition over the whole decay range seems to indicate that the fluorescence observed is to be attributed to the scintillator fluorescence.

The shape of the curves is interpreted as resulting from scintillator monomer emission, and the deviation from exponentiality as the result of dissociation of excited scintillator dimers. The possibility of triplet formation and interaction within spurs is discussed utilizing the prescribed diffusion model.

Factors Relevant to a Short Fluorescence Lifetime of an Aromatic Molecule: Empirical Data†

I. B. BERLMAN

From theoretical consideration, the natural fluorescence lifetime τ_0 of an aromatic molecule is inversely proportional to $n^2 \nu_0^2 \int \epsilon \, d\nu$ where n is the index of refraction of the solvent, ν the wavenumber, ν_0 the wavenumber of the $0 \rightarrow 0$ transition, and ϵ the decadic molar

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† Work performed under the auspices of the U.S. Atomic Energy Commission.

extinction coefficient. If $\Delta n \approx 0$ and $\int \epsilon \, d\nu$ is replaced by $\epsilon_{\max} \Delta\nu$, where the half-width $\Delta\nu$ of an absorption band is assumed to be approximately the same for all molecules and $\epsilon_{\max}$ is the maximum value of the molar extinction coefficient then it follows that τ_0 is inversely proportional to $\nu_0^2 \epsilon_{\max}$. In this study, the variation in n has been minimized by using cyclohexane as the solvent in all solutions.

A formula developed by Förster was used to compute τ_0 for more than seventy aromatic molecules, and curves of τ_0 versus $\nu_0^2 \epsilon_{\max}$ and τ_0 versus $\epsilon_{\max}$ were drawn. The empirical data appear to confirm theoretical predictions that the shortest fluorescence lifetime is about 1 nsec.

The term "natural fluorescence lifetime" implies a quantum yield of 1.0. In those cases in which the quantum yield is less than 1.0 as a result of internal or external quenching processes, the observed fluorescence decay time τ can be shorter than 1 nsec by more than one order of magnitude. For an exponential fluorescence decay, it follows that $\tau = \tau_0 Q$ and that τ is directly related to Q.

The Effects of Oxygen Quenching on the Time Response of Liquid Organic Scintillators

E. C. YATES, D. G. CRANDALL and J. KIRKBRIDE

The time response of liquid organic scintillators can be significantly improved by the addition of oxygen. Precision measurements† of the scintillation decay curves of several oxygen quenched organic liquids have been made. The fastest decay constant obtained was $\tau = 1.65$ nsec with NE211. Dissolved oxygen almost completely eliminates the long tail components of the scintillation, and only reduces the peak output light by about 50%. In addition, the effects of dissolved nitrogen were also examined. In general, nitrogen increases the tail and peak light outputs.

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† McGuire, R. L., Yates, E. C., Crandall, D. G. and Hatcher, C. R. "Apparatus for Precise Measurement of Scintillator Decay Times", *IEEE Transactions on Nuclear Science* NS-12, Feb. 1965, pp. 24–27.

Pathways of Triplet–Triplet Annihilation in Ethanolic Solutions of Pyrene

B. STEVENS and M. I. BAN

The observation of both molecular and excimer bands in the delayed fluorescence spectrum of dissolved pyrene (A) led Parker and Hatchard[1] to suggest that triplet–triplet annihilation in this system involves the prior formation of an excimer A_2^*, the sequence of events being represented by

$$\begin{tikzcd}
{}^3A + {}^3A \arrow[r, "1"] & A_2^* \arrow[r, shift left] \arrow[d] & A^* + A \arrow[l, shift left] \arrow[d] \\
& 2A + h\nu_D & A + h\nu_M
\end{tikzcd}$$

where A^* and ${}^3A$ denote lowest excited molecular states of singlet and triplet multiplicity.

This scheme is consistent with the observed negative temperature coefficient of excimer/molecular band intensities D_D/D_M in the delayed emission spectrum recorded at higher temperatures ($>20°$ C), since excimer dissociation requires an activation energy of ~ 10 kcal/mole.[2] However, at lower temperatures the intensity ratio D_D/D_M exhibits a positive temperature coefficient, and at $-196°$ C no excimer band is observed. To account for this behaviour Tanaka *et al.*[3] proposed the additional process

$$ {}^3A + {}^3A \xrightarrow{2} A^* + A \rightleftarrows A_2^* $$

which may occur at distances greater than those defining the molecular encounter necessary for process 1.

From an analysis of the relevant fluorescence parameters Birks[4] finds that the ratio of rate constants $k_1/k_2 = 2.02$ in ethanolic solution at room temperature. If process 1 is diffusion-limited and process 2 is long range and viscosity-independent, this ratio should have a positive-temperature coefficient at lower temperatures. Measurements of D_D/D_M and of the excimer/molecular band intensity ratio F_D/F_M in the normal fluorescence spectrum as a function of temperature in the range 200–250° K show that k_1/k_2 is independent of temperature, in which case process 2, like process 1, is diffusion-limited. These processes are discussed.

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Charge-Transfer Exciton State, Ionic Energy Levels, and Delayed Fluorescence in Anthracene

M. POPE

Our work on the delayed electroluminescence of anthracene crystal has shown that the recombination of holes and electrons produces the normal fluorescence of anthracene, and that the time dependence of the fluorescence can be modified by an external electric field. We have also shown that the recombination of holes and electrons produces an ion-pair or charge-transfer (CT) exciton, that this CT exciton diffuses through the anthracene crystal, and can form a dimer with another CT-exciton; the decay of the dimer produces one photon, at most. The normal decay of the nearest neighbor CT exciton, and the CT-exciton dimer produces a tail that extends into the microsecond region. Some estimates are given for the lifetime and the diffusion length of the CT exciton; ionic energy levels for anthracene crystal are also given.

Lifetime and Diffusion Length of Excitons in Naphthalene Crystals

A. HAMMER, T. B. EL KAREH and H. C. WOLF

The fluorescence of pure naphthalene crystals has two origins at 31,475 and 31,625 cm^{-1}, which correspond to the two Davydov-components of the lowest singlet exciton band. Therefore one expects *two decay times* for the naphthalene fluorescence. In order to find these times we measured the decay of naphthalene fluorescence as a function of crystal thickness and temperature. Apparently the measured decay time of 110 nsec at 4° K (thick crystals) is the lifetime of excitons in the *lower* Davydov-component. The measured value of 114 nsec at room temperature (thick crystals) belongs mainly to the higher Davydov-component. Taking into account the effect of reabsorption, one gets an estimated value of 40 nsec for the radiative lifetime of the ***higher*** exciton band. The measured decay times of very thin crystals (below 100 μ) at low temperatures are shorter than expected.

Diffusion of excitons to the surface cannot explain this discrepancy. The product DR (D = diffusion coefficient, R = trapping radius for excitons of the anthracene impurity) is measured in the system naphthalene/anthracene as $\simeq 10^{-11}$ cm^{3}sec. Taking R = 10 Å one gets an estimated value of 300 Å for the *diffusion length* of singlet excitons in naphthalene crystals. This diffusion length increases with decreasing temperature in a manner which can be explained as a consequence of scattering of excitons on phonons. We have experimental evidence for the increase of energy transfer efficiency with decreasing temperature.

Migration of Triplet Excitons in Molten Naphthalene

H. BÄSSLER

Illumination of zone refined molten naphthalene by a Xenon-arc lamp produces a photocurrent, if an electric d.c.-field is applied (with all experiments the direction of the incident light was parallel to the electrodes). The spectral response curve shows one maximum at the wavelength of the forbidden S_0–T_1-absorption band and a stronger one at the longwave edge of the S_0—S_1 absorption. Generally the photocurrent is proportional to the light intensity. No effect can be observed if blocking quartz electrodes instead of gold electrodes are used. It is concluded that light produces triplet excitons in the bulk of the dielectric, which can diffuse to the anode. From energetic reasons it is possible that they dissociate there into an electron and a cation. The electron is received by the anode, the cation can migrate to the cathode and produce a photocurrent.

The model can be checked experimentally by variation of the distance of the illuminated volume layer from the anode. It is verified that a Gaussian diffusion profile for the excitons exists. Furthermore the diffusion length L and the diffusion constant D can be estimated. One obtains the surprisingly large values $L \approx 1$ cm, $D \approx 1$ cm^2/sec. Small amounts of triplet traps or triplet quenchers can reduce L. They either act in slowing down the mean velocity of the triplet excitons or in reducing their mean lifetime.

The results indicate that triplet-energy transfer in molten aromatics occurs more rapidly than in crystals.

Fluorescence of Liquid Scintillators at High Temperatures

M. FURST, H. KALLMANN and E. LEVIN

A study of effects of temperatures above ambient (300–550° K) on liquid scintillators is being carried out.† Measurements of fluorescent intensity at different solute concentration yield values of Q and of P/R in the scintillator formula: $I = Pc/(Q+c)(R+c)$. P/R is related to the fluorescence efficiency which is found by direct solute excitation with UV light. The Q value is determined by measuring I versus concentration under conditions of energy transfer from the excited solvent.

It has been found that the fluorescence efficiency of many solutes decreases moderately with increasing temperature; PBD shows no decrease until about 500° K. Under energy transfer conditions, it is found that the number of states (of the excited solvent) which can transfer energy to the solute is roughly independent of temperature. The parameter Q, which is related to transfer efficiency, is found to increase considerably with temperature; this is correlated with the fluorescence efficiency of the solvent under gamma-ray excitation (η). In general, $Q\eta$ is found to be constant. This is interpreted to mean that Q is essentially determined by the solvent fluorescent lifetime. In anisole, the change in fluorescence is mark-

† International Symposium on Luminescence, Munich, Germany, September 1965.

edly different from many other solvents. The feature of interest is the increase of fluorescent intensity with increasing temperature, up to about 400° K; this may be due to the strong dimer formation in anisole, which decreases as the temperature is raised.

Energy transfer was also investigated under conditions where the solvent was excited by UV light, rather than by gamma rays. In most of these cases, the temperature variation of fluorescence was similar to gamma-ray excited case. However, especially in cumene solution, the behavior was decidedly different, indicating that higher excited states may be involved.

Delayed Luminescence of Organic Mixed Crystals†

M. KINOSHITA and S. P. McGLYNN

The delayed luminescence spectra and decays of the guest species in the following mixed crystal systems have been investigated extensively: naphthalene-h_8 in biphenyl; naphthalene-d_8 in biphenyl; phenanthrene in biphenyl; and chrysene in biphenyl.

The kinetic model used here is identical to that proposed by Sternlicht, Nieman and Robinson, and by Azumi and McGlynn:

$$\begin{array}{lll}
(0) & S_0 \rightarrow S_1 & R_0 \\
\begin{array}{l}(1)\\(1)'\end{array} & \begin{array}{l}S_1 \rightarrow S_0 + h\nu\\ S_1 \rightarrow S_0\end{array} & \left.\begin{array}{l}k_1^*\\ k_1\end{array}\right\} k_1^* + k_1 = K_1 \\
(2) & S_1 \rightarrow T_1 & k_2 \\
\begin{array}{l}(3)\\(3)'\end{array} & \begin{array}{l}T_1 \rightarrow S_0 + h\nu\\ T_1 \rightarrow S_0\end{array} & \left.\begin{array}{l}k_3^*\\ k_3\end{array}\right\} k_3^* + k_3 = K_3 \\
(4) & T_1 + T_1 \rightarrow S_1 + S_0 & K_4 \\
(5) & T_1 + T_1 \rightarrow T_1 + S_0 & K_5
\end{array}$$

For the processes (4) and (5), we assume a thermal activation, ΔE, of the guest triplet state to one of its vibrationally excited states comparable with the energy of the host triplet exciton band.

We obtain the expressions for the delayed luminescence intensities, $(I_0)_P$ and $(I_0)_{DF}$, and for their decay behaviors, $(I/I_0)_P$ and

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† Research supported by the U.S. Atomic Energy Commission—Biology Branch.

Quantity	Expression	Range of K^{a}	Approximate expression	I_{ex} ᵇ dependence	Temp (T) dependence	Concentration (C) dependence
$(I_0)_P$	$\frac{k_3^* K_3}{2k_6}[(1+4K)^{1/2}-1]$	$K \ll 2$	$\frac{k_3^* k_2 R_0}{(K_1+k_2) K_3}$	I_{ex}^1	independent	C^1
		$K \gg 2$	$k_3^* \left[\frac{k_2 R_0}{(K_1+k_2) k_6}\right]^{1/2}$	$I_{ex}^{1/2}$	$\exp(+\Delta E/2kT)$	$C^{1/3}$
$(I_0)_{DF}$	$\frac{k_1^* K_4}{K_1+k_2}\left[\frac{K_3}{2k_6}[(1+4K)^{1/2}-1]\right]^2$	$K \ll 2$	$\frac{k_1^* k_2^2 K_4 R_0^2}{(K_1+k_2)^3 K_3^2}$	I_{ex}^2	$\exp(-\Delta E/kT)$	$C^{7/3}$
		$K \gg 2$	$\frac{k_1^* k_2 K_4 R_0}{(K_1+k_2)^2 k_6}$	I_{ex}^1	independent	C^1
$\frac{(I_0)_{DF}}{(I_0)_P^2}$	$\frac{k_1^* K_4}{(K_1+k_2) k_3^{*2}}$		independent of K	Independent or log $(I_0)_{DF}$ versus log $(I_0)_P$ plot gives slope of 2	$\exp(-\Delta E/kT)$	$C^{1/3}$
Decays		$K \ll 2$	$\exp(-K_3 t)$	$\tau_P = 2\tau_{DF}$		
$(I/I_0)_P$ or $(I/I_0)_{DF}^{1/2}$	$\frac{1-A}{\exp(K_3 t)-A}$	$K \approx 2$	$\left(1+\frac{K_3}{1-A}t\right)^{-1}$ $(t \ll K_3^{-1})$	2nd-order	1st-order for $t \gg K_3^{-1}$	
		$K \gg 2$	$(1+K^{1/2} K_3 t)^{-1}$ $(t \ll K_3^{-1})$	2nd-order	1st-order for $t \gg K_3^{-1}$	

$(I/I_0)_{DF}$, which are tabulated opposite. Other constants used in the table are defined as:

$$k_6 = K_4(2K_1+k_2)/(K_1+k_2)+K_5,$$
$$K = k_2 k_6 R_0/(K_1+k_2) K_3^2,$$
$$A = [(1+4K)^{1/2}-1]/[(1+4K)^{1/2}+1].$$

Almost all the predictions have been verified experimentally.

Quantum Efficiencies of Triplet Formation in Aromatic Molecules†

M. W. WINDSOR and W. R. DAWSON

Quantum efficiencies of intersystem crossing ϕ_T from the first excited singlet state, S_1, to the lowest triplet state, T_1, have been measured for several aromatic hydrocarbons. The measurements were made in rigid glass solutions at liquid nitrogen temperatures. Previous attempts to measure ϕ_T have been quite indirect. The present method entails a direct measurement of the concentration of triplets produced for a known intensity of excitation light. The excitation intensity is measured by chemical actinometry. In order to obtain the triplet concentration from the observed optical density of the triplet–triplet absorption band, it is necessary to know also the value of ϵ_T, the extinction coefficient for the T–T transition. Values of ϵ_T are obtained from measurements of ground state depletion. Representative values obtained for ϕ_T are: anthracene-d_{10}, 0.53; chrysene, 0.7; picene, 0.36; 1, 2; 5, 6 dibenzanthracene, 0.98; 1, 12 benzperylene, 0.59.

If, in addition to ϕ_T, the sum of the rate constant $(k_F+k_F'+k_T)$ for removal of molecules from the first excited singlet state S_1 is also known, the rate constant k_T for intersystem crossing can be calculated (see Fig. 1). The sum $(k_F+k_F'+k_T)$ is simply the reciprocal of the measured fluorescence lifetime and data for some compounds are available from observations of fluorescence decay following excitation by a nanosecond flash.

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Coupled with a knowledge of fluorescence yield ϕ_F, the above data make it possible to estimate the importance of radiationless transitions between S_1 and the ground state.

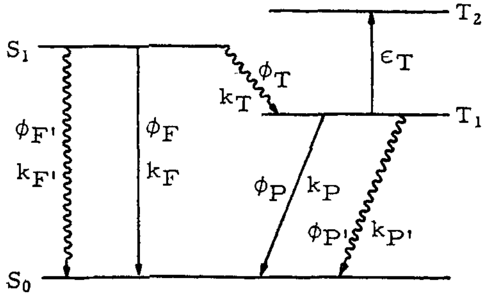

Figure 1. Quantum yields and rate constants in aromatic molecules.

If the quantum yield of phosphoresence ϕ and the measured phosphorescence lifetime τ_P are known, the value of ϕ_T can be used to estimate the true radiative lifetime τ_T of the lowest-triplet state. Since values of τ_P for the perdeuterated molecule set a lower limit on this lifetime, the two values of lifetime can be used to assess the accuracy of the ϕ_P value.

Sensitivity Enhancement for Low-Level Activities by Complete Syntheses of Liquid Scintillation Solvents

M. A. TAMERS

Liquid scintillation counting of low specific activity samples has an important advantage over the conventional gas counter methods in the density of liquids being very much greater than that of gases. In this way, large quantities of material can be compacted into a relatively small space and counted without an excessively high background or inconveniently large shield. The gas counters have backgrounds consistently lower than liquid scintillation counters, but this can be more than compensated for by the larger sample possible in the liquid form.

In order to take full advantage of liquid scintillation measurements for low-level radioactivity, a large part of the solvent should be synthesized from the material of the sample to be counted. This procedure has been applied to three natural radioactivity dating methods. For carbon-14, the most sensitive and practical of the various liquids investigated is benzene. The compound, in addition to being an excellent liquid scintillation solvent, contains 92% carbon. The work on the synthesis of benzene for carbon-14 dating is now complete with yields approaching 100% and less than eight hours total chemical preparation time. Furthermore, the isotope effect for carbon has been proven to be small and reproducible to better than $\frac{1}{2}$%.

A synthesis of benzene for low-level tritium measurements has also been developed. Benzene contains 8% hydrogen, but the synthesis is considerably simpler than that used for radiocarbon dating. Due to the faster chemistry, large quantities of benzene for tritium dating can be produced and the sensitivity increased in this way. An isotope effect of -34% has been observed, but it seems to be sufficiently reproducible not to pose a problem to the use of the liquid scintillation counter for tritium dating.

The possibility of age determinations with naturally occurring chlorine-36 is attractive due to the long half-life of that isotope. Dating of samples with ages of more than a million years is possible. The procedure now being developed consists of the synthesis of an inorganic compound, silicon tetrachloride, from the chlorine of the sample to be dated. The synthesis is rapid and has a yield of better than 75%, but the compound is not suitable for use without the presence of an organic solvent in which the scintillators must be dissolved. Despite this, with silicon tetrachloride much larger quantities than were previously possible can be counted and the method offers promise of eventually making chlorine-36 dating practical.

The chemical and counting procedures of the carbon-14, tritium, and chlorine-36 dating methods are discussed and comparisons made with the gas counters. Liquid scintillation counting is already as sensitive as the best of the other systems and is capable of further significant improvements.

Triplet Sampled Radiation Damage

S. Z. WEISZ, P. RICHARDSON, A. COBAS and R. C. JARNAGIN

The emission produced by mutual annihilation of a pair of triplet excitons in single crystalling anthracence was observed to be an indicator of low level γ-ray dose. Under steady red light illumination the blue emission intensity F_r is related to γ-ray dose D by $F_r^{-1/2} = a + bD$ in the range 300 r to 10^4 r. Independent measurements show the effect cannot be due to changes in absorption in the red region, changes in quantum yield of fluorescence, nor to changes in the specific rate of triplet interaction. An interpretation based on dose induced quenchers and the long range of triplet excitons is given. By use of multiple techniques an individual single crystal of anthracene can be used as a wide range dosimeter; triplet–triplet annihilation in the range 10^2 to 10^4 r, space charge limited photocurrent in the range 10^3 to 10^6 r, fluorescence quenching in the range 10^5 to 10^8 r, and absorption spectroscopy above 10^7 r.

Timing with Organic Scintillators

F. J. LYNCH

The variation of light intensity with time after excitation by gamma rays has been measured for some scintillators by use of a probability sampling technique. Preliminary measurements of $1^2,2^3,3^2,4^3$-tetramethyl-*p*-quaterphenyl (10 g/*l*) and $1^1,4^4$-bis (2-butyloctyloxy)-*p*-quaterphenyl (16 g/*l*.) in p-xylene show an exponential rise and decay with mean lives of less than 0.1 nsec and 1.14 nsec, respectively. When the scintillators are coupled to a photomultiplier with bi-alkali photocathode, the amplitudes of the integrated output pulses are about 50 % greater than that obtained with Naton-136.† The γ–γ delayed coincidence curve obtained

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† Plastic scintillator commonly used for good time resolution, manufactured by Nash-Thompson, Ltd.

with these liquid scintillators has a full width at half maximum of 0.22 nsec for 511-keV γ rays. Theoretical calculations of time resolution, which include the photomultiplier as well as the scintillator parameters, forecast what further reduction in timing uncertainties may be expected from more efficient and faster scintillators and photomultipliers.

Plastic Scintillators from Cross-Linked Epoxy Resins

F. W. MARKLEY

Several attempts have been made to produce a plastic scintillator based on epoxy resins instead of styrene or vinyl toluene. The advantages of such a system are many. The shrinkage on polymerization would be an order of magnitude less than styrene. Combined with low vapor pressure and a smaller exotherm, this would mean that scintillators could be easily cast into complex and readily reproducible shapes. Since the epoxies are cross-linked systems, such a scintillator would have greater dimensional stability, greater resistance to high temperature and to chemical or solvent attack, and essentially no tendency to stress crack or surface craze. It might be possible to operate such scintillators directly immersed in strong solvents which could be very advantageous in many chemical and biological experiments. In addition, epoxy resin systems can be easily tailored for special applications by the addition of modifying agents such as flexibilizers.

Preliminary efforts have produced epoxy scintillators whose pulse height is 60% of Pilot Chemical Company's Scintillator B. The primary difficulties are the chemical reactivity of many conventional scintillators (such as 2,5-diphenyloxazole) toward the Lewis acid cross-linking agents used, and the poor solubility of the nonreactive scintillators such as *p*-terphenyl. It is hoped that recent work on new scintillators of high solubility by H. O. Wirth† will solve these problems.

† Formerly of Johannes Gutenberg Universität, Germany.

Additional efforts must be spent in finding more effective surfactants and diluents to increase the ease of casting with the system. Also investigation must be made of the factors affecting storage of the liquid components in the hope that the system may be kept for long periods of time without degradation, thus eliminating the need to stock assorted sizes and shapes of solid scintillators.

Measurement of the ultraviolet transmission of the best epoxies indicate that they are nearly as good as UVT Lucite which is necessary if they are to be good scintillators in large pieces, unless their output is shifted into the visible region.

It should be emphasized that present work has been done with conventional, commercially available materials. No effort has been spent in purifying, deoxygenating, or otherwise treating, these materials. Commercial prices can, therefore, be used to estimate the cost of the system, excluding the casting, which is about $1.23/lb in large quantities. Future work will investigate impurity effects, but it is apparent that a usable product can be produced without additional purification.

On the Correlations Between Constitution and Scintillation Properties in the *p*-Oligophenylene Series

H. O. WIRTH, F. U. HERRMANN, G. HERRMANN and W. KERN

The paper deals with the problem: What properties are requested from an organic scintillator solute and what structural principles are given to realize, or at least to influence them. According to their importance and also regarding to more or less special purposes one can distinguish the following sequence:

1. An organic scintillator solute must have a sufficient solubility in all types of solvents used for this counting method. Substitution of larger alkyl or oxaalkyl groups has been recognized as an effective and widely generalizable solubilization principle. With

that, one almost can say, all solubility problems are solved, not only those in the field of organic scintillator solutes.

2. In any case a high light output is of greatest importance. In the *p*-oligophenylene series the scintillation efficiency increases with the degree of condensation (number of rings). Substituents disturbing the complanarity cause a decrease in light output.

3. The fluorescence wavelengths should be in a favorable range in order to match the response of the commonly used phototubes. In the *p*-oligophenylene series with increasing degree of condensation the absorption and therefore also the fluorescence bands are shifted into longer wavelengths. Because of the convergence phenomena in connection with the lower accessibility of the higher homologs one reaches scarcely the range of 400 $m\mu$. By introducing other cromophoric systems any desired fluorescence range can be established.

4. For many measurements, especially in high energy physics, a short decay time is of greatest interest. For the *p*-oligophenylene series the decay time decreases as the degree of condensation increases.

Scintillation Measurements at Very High Solute Concentrations

D. L. HORROCKS and H. O. WIRTH

Up to this date very little is known on the scintillation properties of organic systems at very high solute concentrations. Limited solubility had prevented studies of this type.

Compounds are now available with solubilities making possible such studies. They are derivatives of well-known basic substances previously used in scintillation studies. The substitution of larger alkyl groups greatly enhanced their solubility.

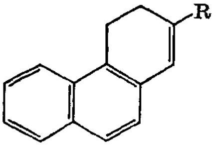
Studies were performed with a series of 1,1′-binaphthyl derivatives and some $1^1,4^4$-dialkyloxy-*p*-quaterphenyls. These results will be discussed. Also a comparison will be made with similar studies with PPO (2,5-diphenyloxazole).

The Synthesis and Evaluation of some *trans*-1, 2-Diarylethylenes as Liquid Scintillators.

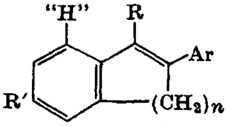
The Steric Effects of a Methyl Group

G. H. DAUB, F. N. HAYES, D. W. HOLTY, L. IONESCU and
J. L. SCHORNICK

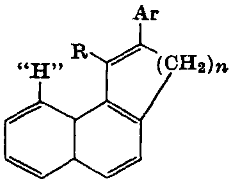
The fact that compounds 1a and 1d were excellent liquid scintillator solutes prompted an investigation of further compounds of similar structure. It can be noted that these compounds cannot undergo *cis/trans* isomerism and the activated forms of these may lose energy in the form of light to return to the ground state; however, if *cis/trans* isomerism is possible (as is the case with *trans*-stilbene) an activated *trans* isomer may revert to the higher energy *cis* form without emission of light. Such a process may be responsible for the very poor showing of *trans*-stilbene as a liquid scintillator solute.



1a, $R = C_6H_5$
1d, $R = 4\text{-}C_6H_4C_6H_5$



2, $R = R' = H$, $n = 1$
3, $R = R' = H$, $n = 2$
4, $R' = H$, $R = Me$, $n = 2$
5, $R' = C_6H_5$, $R = H$, $n = 1$
6, $R' = C_6H_5$, $R = Me$, $n = 1$
7, $R' = C_6H_5$, $R = H$, $n = 2$
8, $R' = C_6H_5$, $R = Me$, $n = 2$



9, $R = H$, $n = 1$
10, $R = H$, $n = 2$
11, $R = Me$, $n = 2$

Compounds 2–11 were synthesized in which Ar equals phenyl (2a–11a), 1-naphthyl (2b–11b), 2-naphthyl (2c–11c), and 4-biphenylyl (2d–11d). These were tested as liquid scintillator solutes in toluene using a 10-channel pulse height analyzer driven by the amplified output of an RCA 6903 quartz-face photomultiplier tube having average S-13 spectral characteristics. Fluorescence spectra in toluene solution and UV absorption spectra were also determined. The relative pulse heights (compared to 3 g of PPO per liter in toluene as 1.00) and fluorescence $\lambda_{\max}$ in mμ are as follows: 2a (0.89, 362), 2b (0.86, 395), 2c (0.73, 395), 2d (0.80 sat., 390), 3a (0.18, 365), 3b (0.88, 390), 3c (0.82, 380), 3d (1.03, 395), 4a (0.0, 375), 4b (0.34, 400), 4c (<0.1, 400), 4d (<0.1, 405), 5a (0.98, 385), 5b (0.95, 405), 5c (0.95 sat., 402), 5d (0.86, sat., 408), 6a (1.09, 385), 6b (0.95, 400), 6c (1.04, 402), 6d (1.02, 410), 7a (0.99, 390), 7b (0.95, 410), 7c (1.01 sat., 405), 7d (0.88 sat., 413), 8a (0.13, 395), 8b (0.83, 415), 8c (0.30, 410), 8d (0.53, 415), 9a (0.83, 395), 9b (0.89, 425), 9c (0.82, 412), 9d (0.92 sat., 420), 10a (0.80, 405), 10b (0.92, 420), 10c (0.90, 415), 10d (1.02, 425), 11a (<0.1, 395), 11b (0.19, 405), 11c (<0.1, 400), 11d (0.1, 410).

Perhaps the most interesting observation regarding the data in the preceding paragraph is that the substitution of a methyl group for the hydrogen on the alkene portion of the molecule where $n = 2$ and the alkene double bond is in a six-membered ring (compounds 4 versus 3, 8 versus 7, and 11 versus 10) has a profound decreasing effect on the pulse height of the scintillator. Molecular models clearly show that such a methyl substituent can effectively twist the adjacent aryl substituent (Ar) out of the plane of the rest of the molecule. The hydrogen atom labeled "H" in the structural formulas above clearly provides a buttressing effect on the steric requirements of the methyl substituent in these compounds.

On the other hand, in the compounds where $n = 1$ and the alkene double bond is in a five-membered ring, substitution of a methyl group for the hydrogen on the alkene portion of the molecule has no effect (or perhaps an increasing effect) on the pulse height (compounds 6 versus 5). Molecular models show much less crowding in such a system and the adjacent aryl group (Ar) can actually assume a planar conformation with the rest of the molecule when the methyl substituent is present.

The Fluorescent and Scintillation Properties of New Oxazoles, Oxadiazoles and Pyrazolines

P. LEGGATE and D. OWEN

The following homologues of POPOP and PDPDP have been synthesised: POBOP, dimethyl-POBOP, BOBOB, dimethyl-BOBOB, POTOP (T = terphenyl), dimethyl-PDBDP, tetramethyl-PDBDP, NDPDN, dimethyl-NDBDN. Two new 4,4-bis (1,5-diphenyl-Δ^2-pyrazolinyl-3)-arenes, in which the arene group is either benzene or 3,3′-dimethylbiphenyl, have also been prepared. The methyl substituents on the aromatic rings greatly enhances the solubility of these compounds. Fluorescent emission and UV absorption spectra, and scintillation efficiencies in both plastic and liquid solutions are reported. The new solutes were evaluated both as wavelength shifters and, where solubility permitted, as primary solutes.

Direct measurements have been made of the self-absorption by the solute of its own fluorescent emission. The implications of the self-absorption data are discussed, both for the determination of "true" scintillation efficiencies for theoretical studies and for evaluating the performance of practical scintillators.

The dependence of spectral and scintillation properties on the length of the conjugated system is examined for the three series of compounds.

A Study of the Quenching Properties of Alcohols in Liquid Scintillator Solutions

A. F. FINDEIS and J. A. LUBKOWITZ

A study has been made of the quenching properties of alcohols in liquid scintillator solutions. The work was done with the purpose of establishing a correlation between the degree of quenching and molecular parameters of the quenching molecules. The investigation was undertaken in order to evaluate quenching properties and apply them in a useful manner. Sixteen alcohols, *n*-C-1 to *n*-C-10, and branched chain alcohols up to C-5 were studied in two of the more common scintillator solutions (toluene and dioxane base), using two isotopes, C-14 toluene, and tritiated toluene. This study extended the work of prior investigators to higher concentrations of quenching molecules and established a generalized order of quenching for these higher concentration ranges. Irrespective of the nature of the composition of the scintillator and independent of the activity monitored, the quenching decreased with increasing molecular weight of the quenching agent. A limited quenching value was approached for normal alcohols above C-6. Branched chain alcohols show a decreasing quenching ability as substitution on the alpha carbon increases. Quenching properties of binary mixtures of the alcohols were intermediate between the quenching curves of the pure alcohols. Five binary systems were evaluated.

The relative quenching behavior of the alcohols was compared with the quenching parameters of compounds containing the same number of carbons but different functional groups. The quenching capabilities of compounds within a homologous series may be interpreted in terms of extended versus coiled configurations of such molecules in solution. The rule of 6 appeared to be a predominating factor in the limiting quenching case of the normal alcohols. The relative quenching order must be specified in terms of concentration units which are consistent and a particular common variable must be evaluated within a homologous series in order to obtain generalized quenching trends. Quenching was not only dependent upon the number of quenching molecules, but also on the steric factors affecting the functional group primarily responsible for the quenching. The significance of the observation of the steric effects on the alpha carbon is that it may play an important role in energy transfer and should be considered, especially, in the light of migration transfer or natural diffusion transfer type mechanisms.

Performance Parameters of some New Efficient and Highly Soluble Solutes for Liquid Scintillators

E. KOWALSKI, R. ANLIKER and K. SCHMID

The limited solubility of many fluorescing organic compounds is known to be a limiting factor in their use as Scintillator Solutes. The solubility can be greatly increased by introducing one or more unbranched or branched alkyl side-chain substituents.†

The results of systematic investigations on unsubstituted and alkyl-substituted benzoxazole, benzoxazolyl-thiophene and 1,3,4-oxdiazole derivatives will be reported. Some of the new compounds proved to be very efficient primary or secondary scintillator solutes with excellent solubilities in toluene. The best among the new primary solutes, the 2-(4′-t-butylphenyl)-5-(4′-biphenylyl)-1,3,4-oxdiazole (butyl-PBD), exhibits a relative photon yield which is 20–25 % higher than that of PPO and comparable to that of PBD known as one of the most efficient primary solutes. Measurements will be discussed indicating that butyl-PBD is much less sensitive to quenching agents than most of the commonly used binary and ternary systems. The wavelength $\lambda_{\max}$ of maximum emission of the butyl-PBD solution is 365 nm, when measured in toluene at a concentration of about 2.10^{-4} mol/l. For internal small-volume counting application in assemblies with aluminium reflector and modern photomultiplier types the use of a secondary solute in combination with butyl-PBD is therefore not necessary.

In the benzoxazol series 2-(4′-biphenylyl)-6-phenyl-benzoxazol, PBBO, was found to be a remarkably efficient secondary solute ($\lambda_{\max} = 395$ nm), which has a solubility of 5 gl.$^{-1}$ in toluene at 25° C.

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† Wirth, H. O., *Proc. Univ. New Mexico Conference on Organic Scintillation Detectors*, TID-7612, Washington, 1961, p. 78.

Anliker, R., "Zum Problem der Löslichkeit bei organischen Szintillator-Soluten", *Internat. Symp. on Luminescence. The Physics and Chemistry of Scintillators*, ed. Riehl, N. and Kallmann, H., Munich, 1966.