

TOWARDS AN UNDERSTANDING OF THE SCINTILLATION PROCESS
IN ORGANIC MOLECULAR SYSTEMS

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Introduction. My interest in organic scintillators began just 25 years ago, and I have been interested in them ever since. Silver jubilees are rare occasions. I propose to celebrate this particular anniversary by departing from the usual pattern of review papers and restricting this talk to an account of my own personal voyage of discovery. There have been many other contributors to the field, and accounts of their work are to be found in my books [1-5] and other review articles [6-23] .

The story opens in 1948 in the Department of Natural Philosophy at the University of Glasgow where I was completing my Ph.D. studies on the microwave properties of ferromagnetic materials. All my colleagues were engaged in research related to nuclear physics, and Professor P. I. Dee suggested that I should seek a suitable project in this area and join the "team". In one of the laboratories I found an unusual instrument consisting of a large naphthalene crystal attached to a photomultiplier. Its designer, G. M. Lewis, explained that this was an organic scintillation counter of the type discovered the previous year by H. Kallmann. "Ionizing radiations impinge on the scintillator and produce light flashes or scintillations", he explained. "Why?", I asked. "We don't know", he replied. The next day I informed Professor Dee of my new project, the study of the scintillation process in organic molecular systems. 25 years later I am still working on it. It was a much tougher assignment than I realised, but en route there has been a lot of interesting physics. We've found answers to many of the original questions, and in turn we've uncovered many new questions that we didn't know existed.

Organic crystals. Kallmann's first organic scintillator (1947) was a naphthalene crystal, grown from moth-balls

bought in a chemist's shop in war-ravaged Berlin. In 1948 P. R. Bell reported that crystalline anthracene had a scintillation yield about 5 times that of crystalline naphthalene. 25 years later crystalline anthracene remains the most efficient organic scintillator in general use. Unfortunately it cannot be grown in such large crystals as naphthalene.

It was to overcome this limitation that I decided to study the scintillations from naphthalene crystals containing different small concentrations of anthracene [24]. There is an efficient solvent-solute energy transfer process in organic crystal solutions due to exciton migration and transfer, and above a certain anthracene concentration the scintillation yield equals and even exceeds that of a pure anthracene crystal. Because of the elimination of the self-absorption which occurs in anthracene crystals [65], mixed organic crystals have the highest scintillation yields of any known organic molecular systems [10]. Moreover they can readily be grown in volumes as large as pure naphthalene crystals.

Despite these virtues mixed organic crystals have found little practical application, because of the parallel discovery of two more convenient types of organic solution scintillator. M. Agno, M. Chiozzotto and R. Querzoli discovered organic liquid solution scintillators in 1949, and in 1950 M. G. Schorr and F. L. Torney found the first organic plastic solution scintillators. Although organic liquid and plastic solutions have lower scintillation yields than organic crystal solutions, they suffer from no limitations of size and shape. Huge sheets and massive blocks of plastic scintillator are used in high energy physics and whole-body counting, and kilolitre tanks of liquid scintillator are used in cosmic ray and neutrino research. There is no need to remind this Symposium of the advantages of liquid scintillators for the direct incorporation and assay of radio-active specimens using the internal counting technique.

Scintillation response. The next topic which I decided to study was the relative scintillation response to different types of ionizing radiation. The scintillation response of an organic scintillator to 5 MeV α -particles is only about 10 per cent of that to β -particles of the same

energy. This effect, which is common to all organic scintillators, is an example of what is known as the L.E.T. (linear energy transfer) effect by the radiation chemists and biologists [31-2].

It was discovered [25] that for β -particles the scintillation response L is proportional to the particle energy E , but that for α -particles L is proportional to the particle range r . Expressed alternatively, the specific scintillation response dL/dr is proportional to the specific energy loss dE/dr when the latter is low as for β -particles, but dL/dr is constant and independent of dE/dr when the latter is high as for α -particles. A theory was proposed [27,28] to account for the effect, leading to a relation of the form

$$\frac{dL}{dr} = \frac{S(dE/dr)}{1 + kB(dE/dr)} \quad (1)$$

At low dE/dr , $dL/dr = S(dE/dr)$, where $S = dL/dE$ is the scintillation yield for β -particles. At high dE/dr , $dL/dr = S/kB = \text{constant}$, as observed. The excited molecules of specific concentration $S(dE/dr)$, responsible for the scintillation, are considered to be quenched with a probability k by ionized or damaged molecules of specific concentration $B(dE/dr)$ produced by the ionizing particle. The parameter kB was determined for an anthracene crystal from observations of the scintillation response to β -particles and α -particles, and relation (1) was used to predict the response to protons and other ionizing particles (Figure 1). Relation (1) applies to all types of organic scintillator, although the values of kB depend somewhat on the nature of the crystal or solvent.

It was thought that molecules permanently damaged by the ionizing radiation might be responsible for the ionization quenching, and a study was therefore made of the deterioration of the scintillation yield of anthracene crystals under prolonged α -particle irradiation [26]. Although the results showed that permanent quenching centres are produced by the irradiation, and that this can be used as a method of radiation dosimetry, the magnitude of the effect is much too small to account for the ionization quenching effect (1). Recent studies have confirmed that molecular ions are the entities responsible for the quenching of the singlet excited molecules which yield the

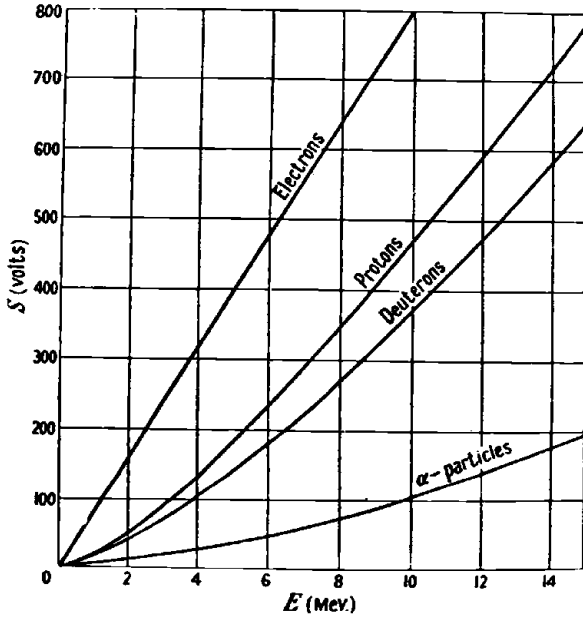


Figure 1. Predicted scintillation response $S(\equiv L)$ of anthracene crystal to particles of energy E [27].

scintillation photons.

A deviation from relation (1) was observed for short-range ($<$ a few μm) α -particles and low-energy external electrons [29]. An analysis showed that the scintillation efficiency is reduced in the surface layer of the scintillator, an effect attributed to surface quenching of the excitation [30]. As a test of this theory, observations were made of the scintillation response of an anthracene crystal to 6-30 keV photoelectrons generated internally by characteristic X-rays [34,36]. The scintillation response is consistent with relation (1), and it is significantly greater than that with external electrons.

To complete these studies the absolute scintillation yield of crystalline anthracene for α -particles was determined, and the corresponding value of S for β -particles was evaluated [33]. The value of $S = 0.04$ compares satisfactorily with those of other observers [2], although later observations on other scintillators suggest that the true value may be as high as $S = 0.06$.

Fluorescence spectra and lifetimes. The later phase of these studies was undertaken during 1951-4 in the Department of Physics, Rhodes University, South Africa. By this time a distinction could be drawn between the primary scintillation processes, associated with ionization, excitation, ion recombination, ionization quenching and radiation damage, and the secondary scintillation processes, associated with internal conversion, energy migration, energy transfer, and fluorescence [8, 9, 12]. The secondary processes can be more readily observed using non-ionizing ultraviolet radiation for excitation, and a programme to study the photophysics of aromatic molecular systems was therefore initiated.

Studies were made of the fluorescence spectra of a wide range of aromatic crystals [48-50], and these were subsequently extended to include scintillator solvents [93] and solutes [19,52]. A direct experimental comparison of the β -particle-excited scintillation spectrum and the optically-excited fluorescence spectrum of several typical organic solutions showed the spectra to be independent of the means of excitation [38].

Similar studies were made of the fluorescence lifetimes of organic crystals [59,60,97] and of organic molecules in solution [61,63,86-7,96]. The techniques used for the determination of fluorescence lifetimes have included phase and modulation fluorometry [59,63,86,130], pulse-sampling fluorometry [60-1, 86-7, 96-7, 108] and the single-photon technique [17,43]. A theoretical and experimental study was made of the relations between the fluorescence lifetime and the absorption and fluorescence spectra of organic molecules [63]. These and other studies of the fluorescence lifetimes of aromatic molecules have been reviewed elsewhere [15].

The scintillation and fluorescence lifetimes of anthracene crystals were shown to be identical, provided that the relatively large effect of self-absorption is taken into account [37,62,65]. In a later paper [79] it has been proposed that the self-absorption in anthracene crystals is due to crystal defects, which act as exciton traps, and the influence of these traps on the fluorescence behaviour of pure and mixed crystals has been analysed.

Energy transfer. Electronic excitation energy transfer is a key process in all solution scintillators. One of the last studies at Rhodes University was of solvent-solute energy transfer from toluene to p-terphenyl by observations of the fluorescence excitation spectra [67]. It was found that the energy transfer rate exceeds that of a diffusion-controlled collisional process, a point to be discussed later.

This work was resumed in 1957 on my appointment at the University of Manchester after a brief spell in industry. A study was made of solvent-solute transfer in plastic solution scintillators [69]. This showed that there is a small radiative transfer component, limited by the fluorescence quantum yield of the polystyrene solvent, and a larger radiationless transfer component which dominates at high solute concentrations (Figure 2). The latter is due to dipole-dipole interaction, the theory of which was formulated by Th. Förster. The probability of energy transfer from a stationary excited donor molecule $^1M^*$ to a stationary acceptor molecule 1Y is given by

$$k'_{YM} = \frac{1}{\tau_M} \left(\frac{R_0}{r} \right)^6 \quad (2)$$

where τ_M is the $^1M^*$ lifetime in the absence of 1Y , r is the intermolecular distance, and R_0 is the Förster critical transfer distance, at which the probability of transfer is equal to the probability of $^1M^*$ decay by other means. R_0 depends on the overlap of the $^1M^*$ fluorescence spectrum and the 1Y absorption spectrum and on the relative orientation of the two molecules. The theory, which only strictly applies to stationary donor and acceptor molecules, agrees satisfactorily with the experimental data on plastic solution scintillators.

Further studies were made of energy transfer between a primary solute (p-terphenyl) and a secondary solute (tetraphenylbutadiene) in a low viscosity solvent (toluene) [70]. The results (Figure 3) show that for the particular specimen thickness of 13 mm, radiative transfer is dominant except at the highest concentrations of secondary solute.

The experimental value of $R_0 = 42.2 \text{ \AA}$ for TP-TPB radiationless transfer in toluene agrees closely with the theoretical value of $R_0 = 42.5 \text{ \AA}$ [70]. This was a surprising result, since the experiments were in a low viscosity solution, while the theory relates to stationary molecules. A series of experiments were therefore undertaken to investigate the influence of diffusion on solute-solute transfer. Energy transfer from anthracene to perylene in benzene solution was studied by measurements of the fluorescence response functions of the donor and acceptor [74]. The fluorescence response functions, defined as the fluorescence quantum intensities as a function of time t following δ -function excitation at $t = 0$ [86], depend only on the radiationless transfer component, and they are unaffected by any parallel radiative transfer. Due to the molecular diffusion in the anthracene-peryene-benzene system, the critical transfer distance is increased from $R_0 = 31 \text{ \AA}$ (for stationary molecules) to $(R_0)_{\text{eff}} = 43 \text{ \AA}$ (in benzene at room temperature).

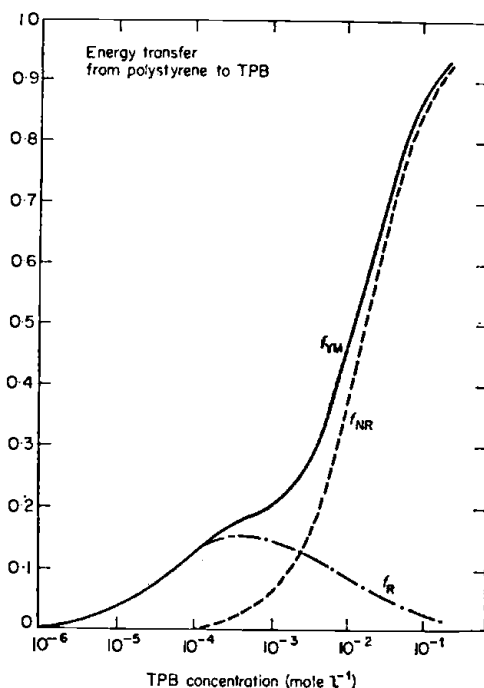
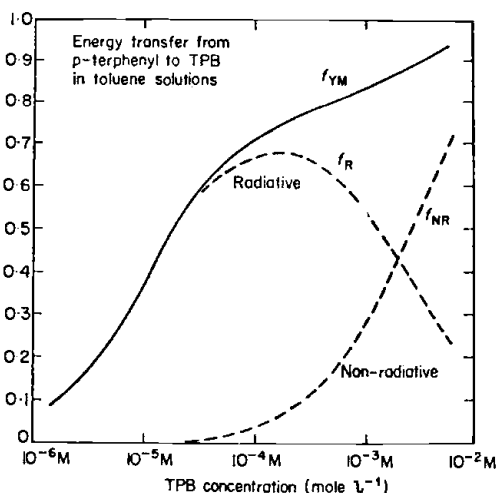


Figure 2. Solvent-solute energy transfer from polystyrene (1M) to tetraphenylbutadiene, TPB (1Y). Energy transfer quantum efficiency f_{YM} , its radiative component f_R and radiationless component f_{NR} against TPB concentration [3, 69].

Figure 3. Solute-solute energy transfer from p-terphenyl ($2.17 \times 10^{-2}M$) to TPB in toluene solution. Energy transfer quantum efficiency f_{YM} , its radiative component f_R and radiationless component f_{NR} against TPB concentration [70].



In a theoretical analysis [75] of fluorescence response functions and scintillation pulse shapes (the two functions are usually identical, since excitation by an ionizing particle is equivalent to δ -function optical excitation) three cases were distinguished, depending on the relative magnitudes of R_0 and the molecular diffusion length $\sqrt{2 D \tau_M}$, where D is the diffusion coefficient.

- (i) $R_0 \gg \sqrt{2 D \tau_M}$. The molecules are effectively stationary during the energy transfer process. The energy transfer is described by Förster kinetics (time-dependent rate parameters) with non-exponential fluorescence response functions.
- (ii) $R_0 \approx \sqrt{2 D \tau_M}$. There is some motion of the molecules during energy transfer. The system is described by intermediate kinetics with semi-exponential fluorescence response functions.
- (iii) $R_0 \ll \sqrt{2 D \tau_M}$. Complete molecular mixing occurs during energy transfer. The system obeys Stern-Volmer kinetics (time-independent rate parameters) with exponential fluorescence response functions.

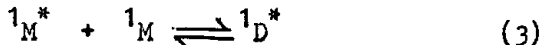
The TP-TPB system in toluene (Figure 3) corresponds to case (i), because of the low value of $\tau_M = 1.2$ ns and the high value of $R_0 = 42.2$ Å.

The transition from case (i) to case (iii) is shown clearly in studies of the fluorescence response functions of phenanthrene ($^1M^*$) in the presence of acridine (1Y) in solvents of different viscosities [64,76]. (Figure 4). In the absence of 1Y the $^1M^*$ decay is exponential. In the presence of 1Y , in a high viscosity ($\eta = 64.6$ cP) solvent the $^1M^*$ decay is non-exponential and agrees with that predicted by Förster kinetics (case i); in low viscosity ($\eta \leq 3.7$ cP) solvents the $^1M^*$ decay is exponential, corresponding to Stern-Volmer kinetics (case iii); and in medium viscosity solvents the $^1M^*$ decay is intermediate between these limits (case ii). A related study of the influence of diffusion on the efficiency of solute-solute energy transfer for various solution systems [78] gave results consistent with the theoretical studies.

In fluid solutions molecular diffusion influences the rate of all bimolecular processes, including solvent-solute energy transfer, solute-solute energy transfer,

impurity quenching, concentration quenching and excimer formation. Naphthalene and biacetyl were chosen as a suitable donor and acceptor system for the study of diffusion-controlled collisional quenching in different solvents, since the Förster radius R_0 for energy transfer from naphthalene to biacetyl is small and it approximates to the sum of the molecular radii [77]. The results of these and related studies have been recently analysed in a comprehensive review of diffusion-controlled rate processes [127].

Excimers. In 1954 Th. Förster and K. Kasper discovered that the concentration quenching of the molecular ($^1M^*$) fluorescence of pyrene in solution is accompanied by the appearance of a new structureless fluorescence band at longer wavelengths. Typical fluorescence spectra of pyrene in cyclohexane solution are shown in Figure 5 [84]. The absorption spectrum is independent of concentration, and the structureless emission is due to excimers ($^1D^*$), i.e. excited dimers which are dissociative in the ground state, formed by the collisional process



For 8 years after the discovery of the pyrene excimer the subject lay dormant, as though the scientific world considered excimer formation to be restricted to the pyrene molecule. In 1962 we decided to look for other aromatic hydrocarbons which formed excimers, and suddenly the subject erupted [81]. Almost every compound that we investigated showed a structureless excimer fluorescence band in concentrated solution, and at one stage new "excimer-formers" were being found at the rate of 2 or 3 a week [81-5, 88]. Many aromatic liquids were found to exhibit dominant excimer fluorescence just above their melting points [89]. Some aromatic crystals also have an intense excimer fluorescence component [50,103]. Within a year or two excimer formation had been shown to occur in practically all aromatic hydrocarbons and their derivatives [11, 20].

Of the condensed polycyclic hydrocarbons with 4 or less rings excimer formation occurs in

- (i) benzene and its alkyl derivatives [93],
- (ii) naphthalene and its methyl and dimethyl derivatives [94],

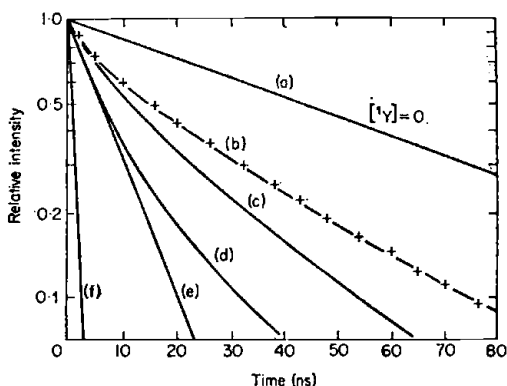


Figure 4. Influence of solvent viscosity η on solute-solute energy transfer from phenanthrene (1M) to acridine (1Y). Donor ($^1M^*$) fluorescence decay curves.

- (b) $\eta = 64.6$ cP; + expt; solid curve, theory;
 (c) $\eta = 27$ cP; (d) $\eta = 10$ cP; (e) $\eta = 3.7$ cP;
 (f) $\eta = 0.4$ cP [76].

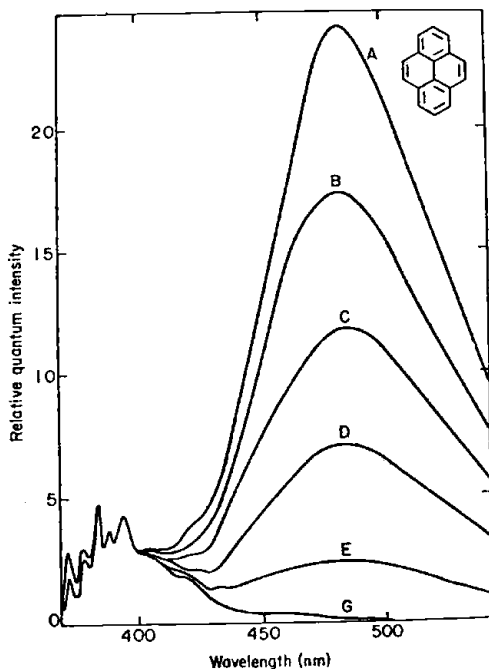


Figure 5. Fluorescence spectra of pyrene solutions in cyclohexane. Intensities normalized to a common molecular fluorescence quantum yield Φ_{FM} . A, 10^{-2} M; B, 7.75×10^{-3} M; C, 5.5×10^{-3} M; D, 3.25×10^{-3} M; E, 10^{-3} M; G, 10^{-4} M [84].

$$i_M(t) \propto e^{-\lambda_1 t} + A e^{-\lambda_2 t} \quad (5)$$

$$i_D(t) \propto e^{-\lambda_1 t} - e^{-\lambda_2 t} \quad (6)$$

λ_1 , λ_2 and A are functions of $k_M (= k_{FM} + k_{GM} + k_{TM})$, $k_D (= k_{FD} + k_{GD} + k_{TD})$, $k_{DM} [^1M]$ and k_{MD} .

Observations were made of $i_M(t)$ and $i_D(t)$ at different values of $[^1M]$ to determine λ_1 and λ_2 , and hence the rate parameters k_M , k_D , k_{DM} and k_{MD} [86-7]. Typical fluorescence response functions are shown in Figure 6. Observations of the $^1M^*$ and $^1D^*$ fluorescence quantum yields, Φ_{FM} and Φ_{FD} , then enabled k_M and k_D to be split into their radiative components, k_{FM} and k_{FD} , and their radiationless components $k_{IM} (= k_{GM} + k_{TM})$ and $k_{ID} (= k_{GD} + k_{TD})$. Recent observations of the triplet quantum yield as a function of $[^1M]$ have enabled k_{IM} and k_{ID} to be split into their internal conversion components k_{GM} and k_{GD} and their intersystem crossing components k_{TM} and k_{TD} [110]. In this manner all the rate parameters in (4) have been determined experimentally for pyrene and other aromatic molecules in solution.

Similar studies at different temperatures have enabled the frequency factors and activation energies of the temperature-dependent rate processes to be determined [86, 91-2]. The enthalpy ΔH and the entropy ΔS of the excimer formation process have also been evaluated. From an analysis of the fluorescence spectrum of the pyrene crystal excimer, we have determined the excimer interaction potential, and the force constants and zero-point vibrational energies of the ground and excited states of the dimer [101, 103-4, 106]. The potential diagram of the pyrene crystal excimer is shown in Figure 7. The results have been used to explain excimer formation in other aromatic hydrocarbons, and its absence in phenanthrene and chrysene [102].

Excimer formation in the liquid alkyl benzenes is of interest, in view of their use as liquid scintillator

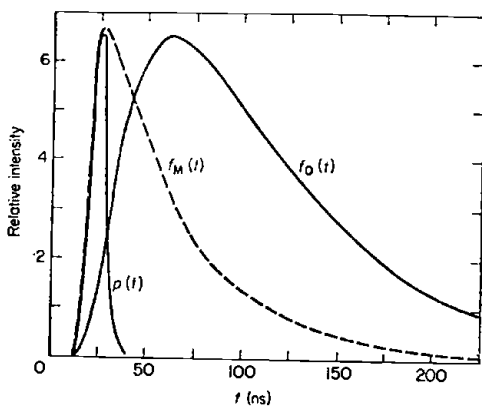


Figure 6. Pyrene (5×10^{-3} M) in cyclohexane solution. Molecular fluorescence response $f_M(t)$ and excimer fluorescence response $f_D(t)$ to excitation light pulse $p(t)$ [86] .

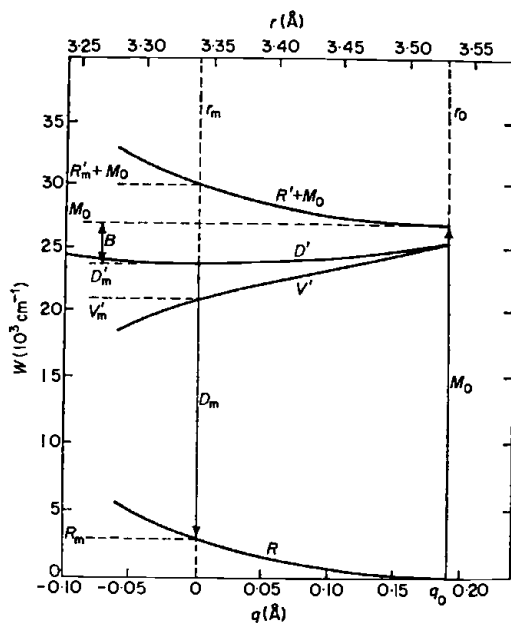


Figure 7. Pyrene crystal dimer and excimer. Potential energy diagram derived from experimental data. Energy (W) against intermolecular separation (r) and displacement (q) from excimer equilibrium [103] .

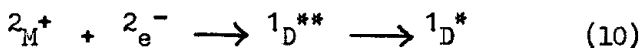
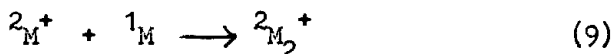
solvents. If liquid benzene, toluene and p-xylene at room temperature are excited optically or by low-intensity ionizing radiation, then 57%, 37% and 14%, respectively, of the excited species are in the excimer state [93, 21]. The excimer fraction d ($= 1 - m$) increases at lower temperatures [107-8]. The excimer formation and dissociation rates, k_{DM} [1M] and k_{MD} , are very high in the alkyl benzenes, and the $^1M^*$ and 1D fluorescences decay at a common rate

$$\lambda_1 = m k_M + d k_D \quad (7)$$

The fluorescence spectrum F of the liquid alkyl benzenes excited optically or by low-intensity ionizing radiation consists of a mixture of the molecular fluorescence spectrum F_M and the excimer fluorescence spectrum F_D [93], so that

$$F = m F_M + d F_D \quad (8)$$

L. G. Christophorou and co-workers discovered that when an intense electron beam is used for excitation, only the excimer fluorescence emission F_D is observed. The effect has been observed in benzene, toluene, the three xylene isomers, mesitylene, and other alkyl benzenes and in alkyl derivatives of naphthalene. The present author [41] has interpreted the effect in terms of the formation and subsequent neutralization of dimer cations

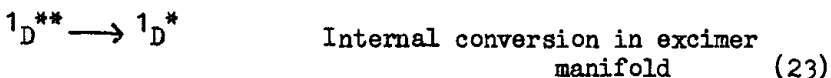
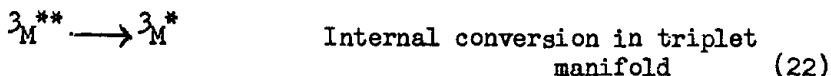
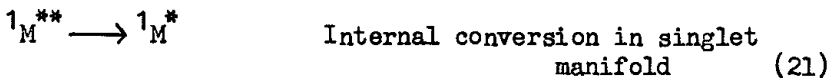
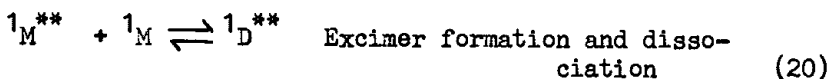
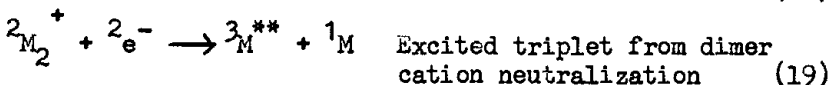
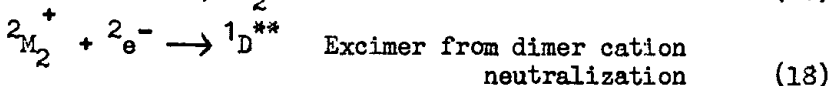
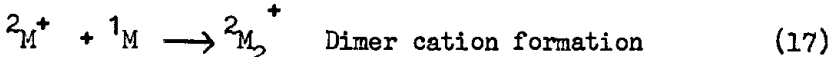
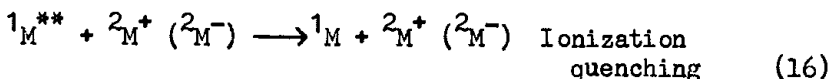
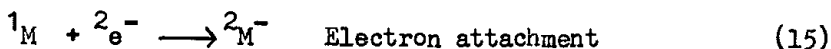
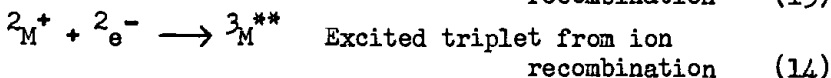
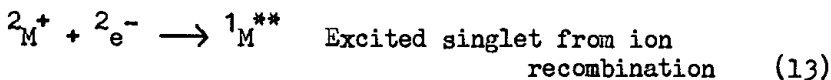
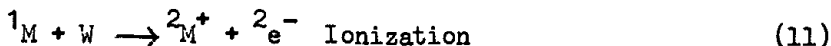


yielding excimers, and the strong ionization quenching of the excited molecules $^1M^*$ which result from dissociation of $1D^*$. It is concluded that excimers are much less prone to ionization quenching than excited molecules.

Primary processes and internal conversion. The primary processes are those by which the energy W dissipated by the ionizing particle in the solvent is converted into molecular ions ($2M^+$, $2M^-$), electrons ($2e^-$), molecules in higher excited singlet states ($^1M^{**}$) and triplet states ($^3M^{**}$), and excimers in higher excited singlet states ($1D^{**}$). The excited species $^1M^{**}$, $^3M^{**}$ and $1D^{**}$ then

undergo radiationless internal conversion and vibrational relaxation into their lowest excited states $^1M^*$, $^3M^*$ and $^1D^*$ respectively.

From various studies [2-3, 9, 21-2] it is concluded that the most important primary and internal conversion processes are as follows.



In an anthracene crystal the $^1M^{**} \longrightarrow ^1M^*$ internal conversion (21) quantum yield $\Phi_{IC} = 1.0$. In the

alkylbenzenes and the polyvinyl alkylbenzenes $\Phi_{IC} \approx 1.0$ for the $^1M^{**} \rightarrow ^1M^*$ (21) and $^1D^{**} \rightarrow ^1D^*$ (23) internal conversion processes [126]. This is one reason why the scintillation yields S of liquid and plastic solution scintillators are less than that of an anthracene crystal. The values of Φ_{IC} are determined from observations of the fluorescence excitation spectra of liquid alkylbenzenes and scintillator solutions [67,126]. For liquid benzene, toluene and p-xylene $\Phi_{IC} = 0.45, 0.76$ and 0.95 , respectively.

A theory of the scintillation yields of liquid scintillators has been developed [22], which takes account of the ionization yield (11) which is inversely proportional to the solvent ionization potential, the singlet excitation yield (12) which is inversely proportional to the mean solvent excitation energy, and the internal conversion yield Φ_{IC} . The theory predicts relative scintillation yields of 82, 100 and 116 for benzene, toluene and p-xylene solutions, respectively, which compare satisfactorily with the observed values of 85, 100 and 112 for 3 gl^{-1} PPO solutions in these three solvents.

The reduced internal conversion yield ($\Phi_{IC} < 1.0$) in the alkylbenzenes and their polyvinyl derivatives is due to a competing radiationless transition which is absent in the higher aromatic hydrocarbons like anthracene where $\Phi_{IC} = 1.0$. The competing process, which is known simply as "channel 3" since its exact nature is uncertain, occurs when the excitation energy is more than $2000 - 3000 \text{ cm}^{-1}$ above the zero-point level of the first excited singlet state ($^1M^*$) of benzene [58]. It corresponds to a fast ($\sim 10^{12} \text{ s}^{-1}$) internal conversion to the ground state (1M) of benzene, and it competes with the $^1M^{**} \rightarrow ^1M^*$ internal conversion which has a similar rate. It has been proposed that the "channel 3" transition occurs via a non-planar "physical isomer" of benzene, which reverts collisionally to the ground state of benzene [58].

"Channel 3" has stimulated fresh interest in the spectroscopy and photophysics of benzene [55, 57, 125] and toluene [108]. From observations [128] of the linewidth of the electronic $S_0 - S_2$ absorption transition

in crystal benzene, extrapolated to 0°K, it is concluded that S_2 has a radiationless decay rate of $9.4 \times 10^{12} \text{ s}^{-1}$. This value agrees satisfactorily with that of $9.9 \times 10^{12} \text{ s}^{-1}$ obtained from the $S_2 - S_0$ fluorescence quantum yield ($= 8 \times 10^{-6}$) of liquid benzene at 25°C recently observed by F. Hirayama and co-workers. This is the first time that the lifetime of a higher excited state of a complex molecule has been determined by both linewidth and fluorescence measurements. From comparison with the fluorescence excitation spectrum of crystal benzene, it is concluded [128] that the $S_2 - S_1$ internal conversion rate is $6.6 \times 10^{12} \text{ s}^{-1}$ and that the "channel 3" rate is $2.8 \times 10^{12} \text{ s}^{-1}$.

Triplet-triplet interaction. F. D. Brooks and G. T. Wright, two of my colleagues at Rhodes University, observed that the scintillation pulse shape of an anthracene crystal excited by α -particles differs from that excited by electrons. The discovery that the scintillation pulse shape depends on the specific energy loss dE/dr of the particle led to the development of the pulse shape discrimination (P.S.D.) technique in which organic scintillators are used to distinguish neutrons, which give recoil protons, from γ -rays, which give Compton electrons.

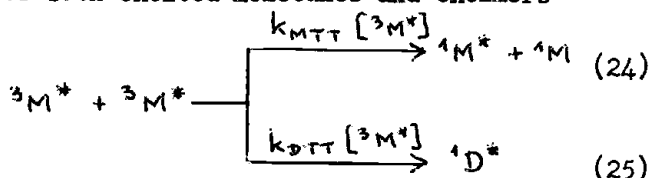
The scintillation decay consists of two components, a prompt component I_p , which decays exponentially, and a delayed slow component I_s , which decays non-exponentially. I_p corresponds to the fluorescence decay of the $^1M^*$ and $^1D^*$ excited species, produced by internal conversion from the $^1M^{**}$ and $^1D^{**}$ excited species (21, 23) generated by the primary processes (12, 13, 18, 20). I_s is due to the bimolecular interaction of the $^3M^*$ excited species, produced by internal conversion from the $^3M^{**}$ excited species (22) generated by the primary processes (14, 19). The rate of the triplet-triplet interaction process



is determined by the $^3M^*$ concentration and diffusion rate, and it produces the delayed $^1M^*$ fluorescence which constitutes the slow component I_s . I_p depends on dE/dr (1), because of the ionization quenching of $^1M^{**}$ (16) but I_s is approximately independent of dE/dr , indicating that the ionization quenching of $^3M^{**}$ is less, possibly

because the $^3M^{**}$ species are only produced by ion recombination. Moreover the process (24) which generates the delayed $^1M^*$ fluorescence is separated in space and time from the primary ionization column. This model [2, 8] accounts reasonably for the scintillation pulse shape and its dependence on dE/dr .

The delayed fluorescence due to triplet-triplet interaction in solution has been studied using optical excitation [113-4, 116-7, 109]. With solute molecules like pyrene, which form excimers, triplet-triplet interaction produces both excited molecules and excimers



The inclusion of these two bimolecular processes in the previous excimer formation and dissociation scheme (4) complicates the kinetic analysis, which has been discussed in detail in Chapter 8 of ref. [3]. Due to process (25) the ratio of the $^1D^*$ and $^1M^*$ fluorescence intensities is greater in the delayed emission than in the prompt emission. This has been used to show that the ruby-laser-excited fluorescence of pyrene solutions is due to two-photon absorption into $^1M^*$, giving the prompt fluorescence spectrum, and not due to one-photon absorption into $^3M^*$, which would give the delayed fluorescence spectrum [95].

Liquid solution scintillators, in the absence of dissolved oxygen, exhibit prompt and slow scintillation components, I_p and I_s , respectively. I_p results from solvent-solute singlet energy transfer



leading to solute ($^1Y^*$) fluorescence. R. Voltz proposed that I_s is due to solvent ($^3M^*$) triplet-triplet interaction (24) followed by solvent-solute singlet energy transfer (26). However the $^3M^*$ lifetime of the liquid alkylbenzenes is only 10-20 ns, while the lifetime of I_s is about 1 μ s. As an alternative to Voltz' model it has been proposed [22, 42] that solvent-solute triplet energy transfer occurs

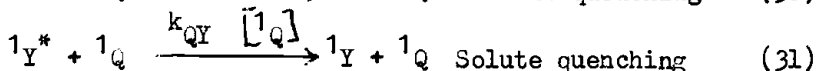
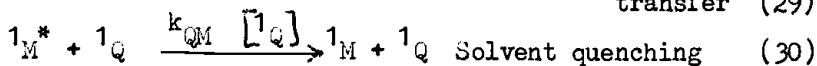
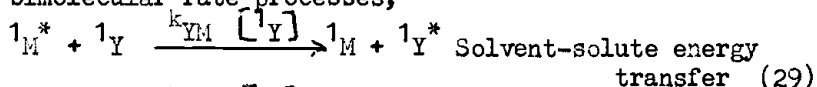


and that the delayed solute fluorescence then results from solute ($^3Y^*$) triplet-triplet interaction



This model is now generally accepted.

Energy transfer and quenching in liquid scintillators. In a liquid scintillator containing excited solvent ($^1M^*$), solute (1Y) and impurity (1Q) molecules, there are three bimolecular rate processes,



Over the last two decades there have been many studies of the solvent-solute transfer process (29) in the author's laboratory [40, 65, 67, 72-3, 80, 126] and elsewhere, and several reviews of the subject have been published [2, 3, 16, 22]. In typical liquid scintillators k_{YM} is independent of whether the solvent is excited by ionizing or ultraviolet radiation, showing that the energy transfer normally occurs from the lowest excited singlet state ($^1M^*$) of the solvent.

The rate parameter of a diffusion-controlled process is given by the Smoluchowski-Sveshnikov relation [3, 127]

$$k_{\text{diff}} = 4 \pi N' D p R \quad (\text{M}^{-1} \text{s}^{-1}) \quad (32)$$

where N' is Avogadro's number $\times 10^{-3}$, D is the sum of the diffusion coefficients of the reactant species, p (≤ 1) is the reaction probability per collision, and R is the molecular interaction distance. A transient term of the order of unity is omitted from (32) to simplify the discussion. Applying (32) to efficient ($p = 1$) solute quenching (31) we obtain

$$k_{QY} = 4 \pi N' (D_Y + D_Q) (r_Y + r_Q) \quad (33)$$

where D_Y and D_Q are the diffusion coefficients, and r_Y and r_Q are the molecular radii of ${}^1Y^*$ and 1Q , respectively. Relations (32) and (33) have been verified for pyrene excimer formation [86], quenching of naphthalene fluorescence by biacetyl in various solvents [77], and quenching of PPO fluorescence by carbon tetrabromide in toluene [80]. In each case R is the sum of the molecular radii and $p = 1$ in room-temperature solution.

The solvent-solute transfer parameter k_{YM} and the solvent quenching parameter k_{QM} each exceed the diffusion-controlled solute quenching parameter k_{QY} by a factor of 2 to 3 [73, 100]. This indicates that

- (i) the effective ${}^1M^*$ diffusion coefficient \bar{D}_M exceeds the molecular diffusion coefficient D_M , and/or
- (ii) the effective ${}^1M^*$ interaction radius \bar{r}_M exceeds the molecular radius r_M ,

so that

$$k_{YM} = 4 \pi N' (\bar{D}_M + D_Y) (\bar{r}_M + r_Y) \quad (34)$$

$$k_{QM} = 4 \pi N' (\bar{D}_M + D_Q) (\bar{r}_M + r_Q) \quad (35)$$

with $\bar{D}_M \geq D_M$, $\bar{r}_M \geq r_M$. In solution systems in which $D_Y \approx D_Q$, $r_Y \approx r_Q$, it is observed that $k_{YM} \approx k_{QM}$, and we have therefore concluded that \bar{r}_M is the same for both processes [100]. The ${}^1M^*$ migration process responsible for $\bar{D}_M > D_M$ reduces the ${}^1M^*$ lifetime of a molecule in the bulk solvent to $\sim 10^{-3}$ that of an isolated molecule, and this reduces the Förster critical transfer distance R_0 to molecular dimensions comparable with the quenching interaction radius [3].

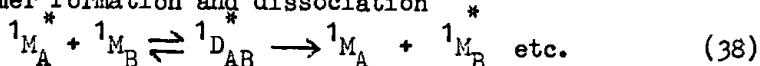
R. Voltz proposed that

$$\bar{D}_M = D_M + \Lambda_M \quad (36)$$

where Λ_M is the coefficient of ${}^1M^*$ migration, due to intermolecular Coulombic and exchange interaction, analogous to exciton migration in an aromatic molecular crystal. With the discovery of excimers in the alkyl benzenes [93], relation (36) was modified to

$$\bar{D}_M = m (D_M + \Lambda_M) + d D_D \quad (37)$$

where m and d are the fractions of solvent excited species in the ${}^1M^*$ and ${}^1D^*$ states, and D_D ($\sim 0.75 D_M$) is the ${}^1D^*$ diffusion coefficient. Birks and Conte [40, 100] proposed that the ${}^1M^*$ migration is due to successive rapid excimer formation and dissociation



where suffixes A and B denote different solvent molecules.

On this model [100]

$$\Lambda_M = d k_{MD} \bar{\alpha}^2 \quad (39)$$

where $\bar{\alpha}$ is the r.m.s. displacement for the ${}^1M_A - {}^1M_B^*$ migration step.

To test these models, observations have been made of the three rate parameters k_{YM} , k_{QM} and k_{QY} for the toluene (${}^1M^*$), PPO (1Y), carbon tetrabromide (1Q) system at temperatures from -20 to $+50^\circ\text{C}$ [80]. The results are shown in Figure 8. The solute quenching parameter k_{QY} agrees satisfactorily with (33). The unexpected result is that k_{YM} (over the full temperature range) and k_{QM} (at $t \leq 20^\circ\text{C}$) are each proportional to k_{QY} . The behaviour of k_{QM} at $t > 20^\circ\text{C}$ is attributed to the factor p , omitted from (35), decreasing below unity.

The observed temperature dependence of k_{YM} and k_{QM} is not consistent with either the Valtz model (36, 37) or the Birks-Conte model (38, 39) of ${}^1M^*$ excitation migration. It is, however, consistent with the relation

$$k_{YM} = 4 \pi N' (\bar{D}_M + D_Q) (\bar{r}_M + r_Q) \quad (34)$$

provided that either

$$(a) \quad \bar{D}_M = 3 D_M, \quad \text{and} \quad \bar{r}_M = r_M, \quad \text{or}$$

$$(b) \quad \bar{D}_M = D_M, \quad \text{and} \quad \bar{r}_M = 3 r_M.$$

In case (a) the ${}^1M^*$ excitation migration coefficient $\Lambda_M = 2 D_M$, and the ${}^1M^*$ interaction radius equals the molecular radius. In case (b) there is no ${}^1M^*$ excitation migration, only diffusion, but the ${}^1M^*$ interaction radius is 3 times the molecular radius, possibly due to excimer interaction (38).

Initially we favoured [80] interpretation (b) since it accounts for k_{YM} and k_{QM} (at $t \leq 20^\circ\text{C}$) each being

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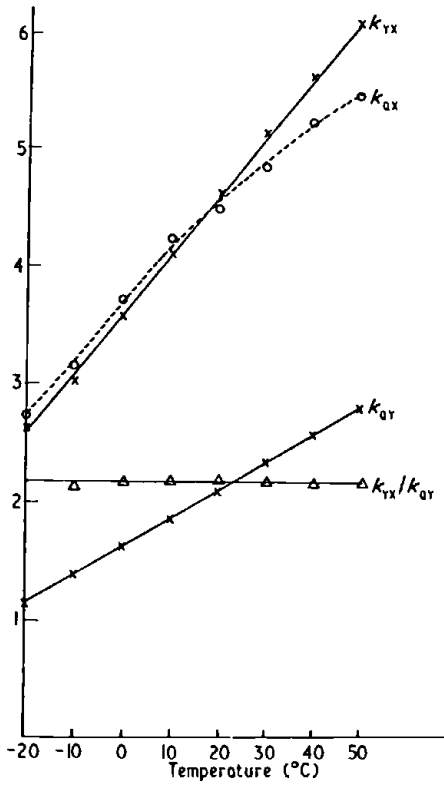


Figure 8. Toluene ($1M^*$) solutions of PPO ($1Y$) and carbon tetrabromide ($1Q$). Rate parameters (in $10^{10} \text{ M}^{-1} \text{ s}^{-1}$) of solvent-solute transfer (k_{YX}), solvent quenching (k_{QX}) and solute quenching (k_{QY}) and k_{YX}/k_{QY} as a function of temperature [80]. ($X \equiv M$)

proportional to the diffusion coefficient. However, in the absence of $^1M^*$ excitation migration ($\bar{D}_M = D_M$), the interaction distance for solvent-solute transfer should exceed that for solvent quenching and k_{YM} should exceed k_{QM} , which is contrary to the observed behaviour. Interpretation (a) does not suffer from these limitations, although a theoretical explanation of the relation

$$\lambda_M = 2 D_M \quad (40)$$

is currently lacking.

Liquid scintillators. Scintillation process studies are made under conditions which differ markedly from those in which liquid scintillators are normally used. Oxygen is usually eliminated from the solutions, since it interferes with several stages of the scintillation process. It captures electrons, it quenches excited singlet ($^1M^*$, $^1Y^*$) and triplet ($^3M^*$, $^3Y^*$) states of the solvent and solute, and it yields singlet-excited oxygen $^1O_2^*$ which is very chemically active [112]. A liquid scintillator at ambient temperature in contact with air contains about $2 \times 10^{-3}M$ of dissolved oxygen, which reduces its scintillation yield by up to 20 per cent. In liquid scintillation counting it is usually considered impracticable or unnecessary to expel the dissolved oxygen.

In scintillation process studies techniques like vacuum distillation, recrystallization, zone-refining, microsublimation and chromatography are used to eliminate impurities. In liquid scintillation counting high purity chemicals may be used to prepare the scintillator "cocktail", but the high scintillation yield thus obtained is partially dissipated by exposure to air, and more drastically by the addition of the specimen and any solubilizing, dispersing, bleaching, diluting or other agents used for its incorporation in the solution [21].

In an attempt to bridge the gap between the theory and the practice of liquid scintillation counting, we have investigated a series of liquid scintillators under practical conditions [23]. The relative pulse heights (RPH) of air-equilibrated solutions at ambient temperature and normal atmospheric pressure were measured using a Philips automatic liquid scintillation counting analyzer. The solutions were contained in standard 20 ml glass vials, and a small quantity of ^{14}C -labelled hexadecane, which is

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a non-quencher, was added to give about 20,000 d.p.m. The RPH values were determined using a "channels-ratio" method.

We used 6 solvents (benzene, toluene, xylene, p-xylene, mesitylene and p-dioxan with 100 g/l naphthalene), 7 primary solutes (TP, PPO, BBOT, PBO, butyl-PBD, PBD and BIBUQ) and 7 secondary solutes (PBBO, POPOP, dimethyl-POPOP, BBO, bis-MSB, α -NPO and DPH). The RPH of the 42 possible binary solution systems were measured as a function of primary solute concentration [Y]. The RPH of 78 ternary solutions based on TP, PPO or PBD in benzene, toluene, xylene or p-xylene were measured as a function of the concentration [Z] of each of the 7 secondary solutes. The results provide a practical guide to the relative performance of 120 liquid scintillator formulations under standard conditions in the absence of the specimen [23].

To simulate the effect of the specimen, we studied the impurity quenching of the RPH of each of the binary solutions due to the addition of carbon tetrachloride [23]. The magnitude of the quenching depends both on the solvent and on the solute. The quenching susceptibility of the solvents increases in the following order: benzene, p-dioxan + 100 g/l naphthalene, toluene, xylene, p-xylene, mesitylene. For the alkyl benzenes this corresponds to the inverse order of their ionization potentials, indicating that the quenching is due to exciplex formation [14, 51]. The quenching susceptibility of the solutes increases in the following order: PBD, butyl-PBD, PBO, BBOT, PPO, BIBUQ and TP. The solutions most resistant to quenching are those in which both the solvent and the solute lie in the early parts of the quenching susceptibility lists.

Table 1, prepared from the experimental data [23], compares the RPH of different binary solutions in the absence (V_0) and presence (V_Q) of 0.1 M carbon tetrachloride. The values of V_Q are expressed relative to $V_Q = 100$ for the PBD-toluene solution, and the values of V_0 are expressed relative to $V_0 = 100$ for the same solution. The values of V_0 may be normalized to the same scale as V_Q by multiplication by 2.73, the quenching factor of the PBD-toluene solution.

Comparison of the values of V_Q and V_0 shows dramatic changes in the relative merits of the solutions due to the quencher. The BIBU_Q-toluene and BIBU_Q-p-xylene solutions, which have the highest V_0 values, have much inferior V_Q values. $V_Q < V_0$ for all the p-xylene solutions, while in contrast $V_Q > V_0$ for all the benzene solutions in the upper part of Table 1. The PBD-toluene solution maintains its superior position in the absence or presence of the quencher.

In liquid scintillation counting the magnitude of the quenching depends not only on the nature of the scintillator, but also on the nature and concentration of the specimen. For those engaged in regular radio-assay of the same type of specimen, the above procedures [23] provide a straightforward method of choosing the optimum scintillator composition under given quenching conditions. For those seeking simpler recipes for efficient liquid scintillators, the values of V_Q (Table 1) determined in the presence of a quencher should prove a more practical guide than those of V_0 determined in its absence.

Conclusion. In keeping with the personal nature of this paper, it concludes with a bibliography of my publications on radiation physics and photophysics. This includes the names of my co-workers at Glasgow, Rhodes and Manchester Universities, to whom I wish to express my appreciation. They have come from all over the world, from Britain, Belgium, Germany, Czechoslovakia, Poland, Portugal, Greece, Cyprus, Iraq, Iran, Pakistan, India, Nigeria, South Africa and the United States, so that what started as a solitary journey has developed into a small international expedition.

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Table 1.

Liquid scintillators. Relative pulse heights in presence (V_Q) and absence (V_0) of 0.1 M carbon tetrachloride.

Solute	Solvent	V_Q	V_0
10 g/l PBD	Toluene	100	100
10 g/l PBD	Benzene	95	77
10 g/l Butyl PBD	Toluene	86	99
10 g/l PBD	p-Xylene	84	96
10 g/l Butyl PBD	Benzene	84	80
8 g/l PBO	Toluene	82	98
8 g/l PBO	Benzene	81	77
10 g/l Butyl PBD	p-Xylene	79	97
8 g/l BBOT	p-Dioxan, 100 g/l naphthalene	77	67
8 g/l PBO	p-Dioxan, 100 g/l naphthalene	75	80
10 g/l Butyl PBD	p-Dioxan, 100 g/l naphthalene	74	72
10 g/l PBD	p-Dioxan, 100 g/l naphthalene	74	70
8 g/l PBO	p-Xylene	70	99
8 g/l BBOT	Toluene	60	79
8 g/l BBOT	Benzene	60	61
15 g/l BIBUQ	p-Xylene	56	103
8 g/l BBOT	p-Xylene	51	79
15 g/l BIBUQ	Toluene	51	103
15 g/l BIBUQ	Benzene	49	79
15 g/l BIBUQ	p-Dioxan, 100 g/l naphthalene	49	82
6 g/l PPO	Benzene	44	58
6 g/l PPO	p-Xylene	44	76
6 g/l PPO	Toluene	44	72
6 g/l PPO	p-Dioxan, 100 g/l naphthalene	35	59
5 g/l TP	Toluene	32	65
5 g/l TP	Benzene	30	52
5 g/l TP	p-Xylene	28	64

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