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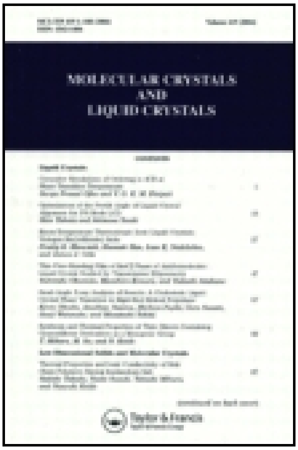

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Liquid scintillators at high temperatures

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Liquid scintillators at high temperatures†

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Abstract—Effects of temperature above ambient (300–550°K) on liquid scintillators are presented. Under excitation by high energy or light usually a reduction in fluorescence with high temperatures is found. However, when excimers are present, a rise may be found. The energy transfer as a function of temperature is studied by means of a theoretical formula, and is found to be greatly temperature dependent. Its dependence is found to be directly associated with variation in fluorescence properties of the solvent by itself.

1. Introduction

Investigation of the effect of raised temperatures on the luminescence properties of organic liquid scintillators has been continued and expanded from that reported previously.[1] The primary concern of this communication is the effect of temperatures up to 250°K above room temperature on energy transfer from the bulk material (solvent) to the emitting substance (solute) under gamma ray and ultraviolet excitation. In some instances the temperature approaches the critical point of the solvent. Earlier work, mostly over a more restricted range and less directly associated with energy transfer, has been reported by a number of investigators, for example: Birks[2], Bowen[3], Galanin[4], Laustriat[5], Umberger[6] and Weinreb[7].

The basic experimental procedure and apparatus has been previously reported[1] in some detail, so that only a brief description will be given here. All solutions were first deaerated to a pressure of 10^{-5} mm of mercury in a vessel consisting of a suprasil quartz section attached to an expansion chamber made of pyrex by means of a graded seal. The measuring cell must be able to withstand pressures of more than 20 atmospheres in some cases because of the high vapor pressures. Effects of heating

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of the photomultipliers (RCA IP28) during the experiment are monitored using an external neon lamp; only slight sensitivity changes are found because the photomultipliers are not in the heating chamber. Three photomultipliers which view the same sample are used. One is used for the gamma ray excitation measurements (PM_1) The other two are used with ultraviolet excitation (mercury source in conjunction with a monochromator) in a manner so that emission is directly viewed at the face where excitation occurs (PM_2), and the other is placed so that the emission is viewed after it has traversed the solution (PM_3).

It has been found in most cases (α-NPO in xylene is one exception) that (PM_2) and (PM_3) give proportional readings showing that there is, rather generally, little or no change in self-absorption upon raising the temperature. Equilibrium measurements of the solution are the only ones considered; normally about one hour has been found necessary for equilibrium to be established when a change of about 20°K is desired. All solutions are tested after cooling to determine whether they return to their original state, indicating that no permanent chemical change occurs during the experiment. Most of the solutions do return but, for example, solutions in p-cymene do not; such solutions are not considered in this paper.

Ultraviolet radiation in two different wavelength ranges was used with the solutions being investigated. In one range the solute was directly excited (3130 Å was used in our solutions); no energy transfer from the solvent occurs under these circumstances. The resulting variation of light output with temperature under these circumstances is thus a measure of solute molecule properties, although the interaction with the solvent may indeed be significant. Data for a number of materials when the solute was directly energized were presented in reference 1. The typical behavior obtained for good scintillating solutions was that of p-terphenyl in o-xylene; first there is practically no change with temperature increases of about 100°K and then there is a fairly rapid decrease in intensity with temperature so that at 520°K the intensity is about one-half that at room temperature. The results are practically independent of concentration. A solution of PBD in o-xylene is atypical in that the variation is much less; the "break" does not occur until about 470°K. The property possessed by PBD of being less affected by its environment (surrounding molecules) has been noted in previous investigations of the effect of quenchers.

2. Solvent Results

The "solvent" when excited with no solute present exhibits a very different behavior. Results under gamma ray excitation and ultraviolet excitation respectively are shown in Figs. 1 and 2 for a number of solvent substances which give good fluorescence. Under both excitations there is a monotonic decrease in emission upon increasing the temperature, except in the case of anisole which is anomalous because of its excimer formation (the relative efficiencies of the monomer and excimer components are different). For a given solvent, the decrease of intensity with temperature is slightly more gradual under UV excitation. This is an indication that the contribution from higher excited states (or ionization) is temperature dependent.

The emission takes place from the lowest excited state but under high energy excitation, a sizeable portion of the population of the lowest state comes from the upper states, whereas under UV only the lowest excited state is energized. It will be seen later that these relative "solvent" radiation efficiencies denoted by η_{sv} are intimately related to energy transfer; this is the case because they are a rather direct measure of the changes of lifetime of the excited solvent molecule.

Excimer presence in anisole is well known[8] and their marked effects in these experiments are not unexpected. It is interesting to note the differences in Fig. 1 between α-methylnaphthalene and anisole. The former is also known to have large numbers of excimers at room temperatures; however, it exhibits a behavior like the other solvents. It is assumed that in both instances the effect of temperature is to reduce the excimer population. The difference in fluorescence behavior between the two substances is brought about by the different relative efficiencies of excimer and monomer emission; in the case of anisole, the monomer is more efficient for radiation, whereas for α-methylnaphthalene it is the excimer which is more efficient.

3. Solution Results

In our previous report,[1] the fluorescence of 2,5-diphenyloxazole in *o*-xylene under 3130Å was described; there the emitting material was more separated in distance from like molecules than in the "solvents" described in Figs. 1 and 2. Up to concentrations of about 10^{-3} m/M there was normal behavior. At high concentrations, in particular 3.7×10^{-2} m/M

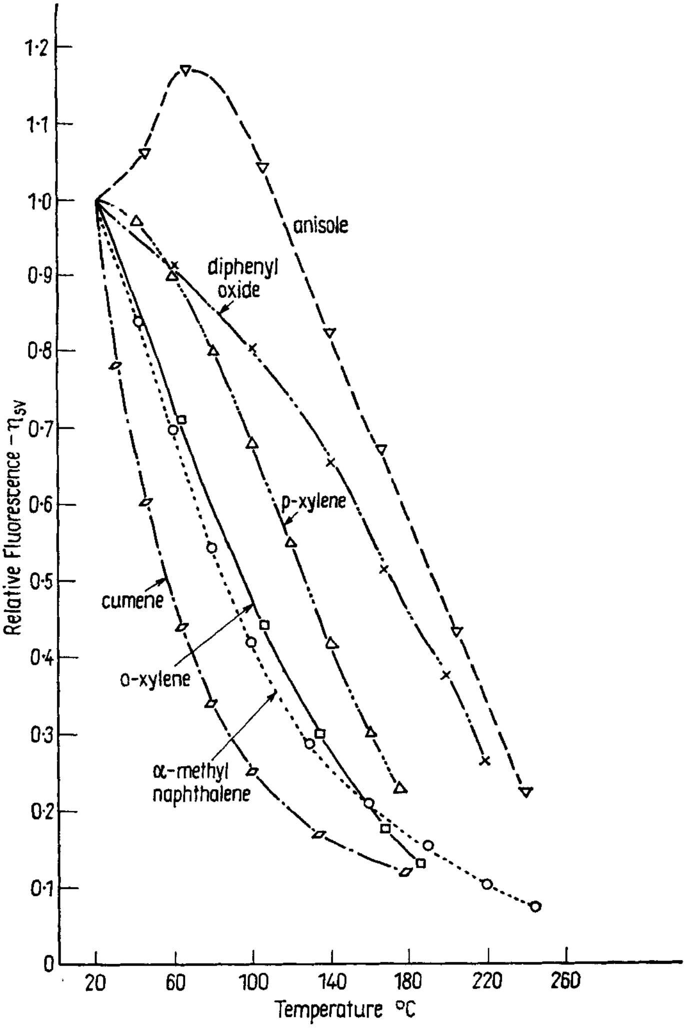

Figure 1. Gamma Ray Induced Fluorescence of "Solvents" at Various Temperatures

where excimers are abundant, the behavior is rather similar to that of anisole, most likely because the monomer is more efficient in emission than is the excimer.

In comparing the results for direct excitation of the emitting molecule for the "solvents" presented in Figs. 1 and 2 with those for dilute solutes, the faster decrease of the "solvent" fluorescence is quite marked.

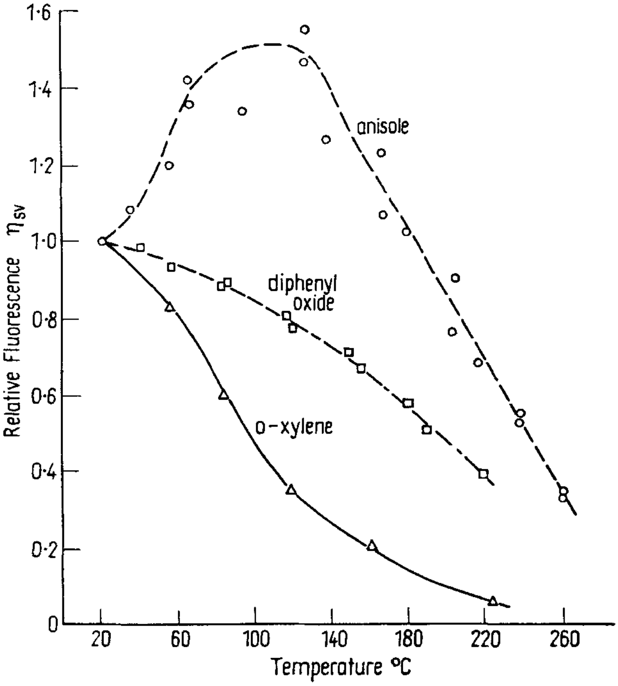

Figure 2. Fluorescence of "Solvents" at Various Temperatures. (Ultraviolet Excitation).

Basically both are similar, but it appears that the environment is significant. If molecules of the same type as the emitter form the surroundings, there is considerable interaction with the surroundings as is evidenced by the large fluorescence change; if the surrounding molecules are different, the interaction appears to be very much smaller. This may be associated with the difference in excitation levels of the two substances but may also be due to geometric orientation factors. It may be noted that the particular form or possible orientation of the molecule is also quite significant in concentration ("self") quenching of solute molecules.[10]

The major interest in this work, as has been pointed out, is the effect of temperature on energy transfer from the solvent to the solute. In order to study this, the behavior of solutions when the solvent is excited is studied for different solute concentrations. Fairly typical results of this kind of experiment normalized to unity at room temperature for all concentrations are shown in Fig. 3 for PBD in o-xylene under gamma

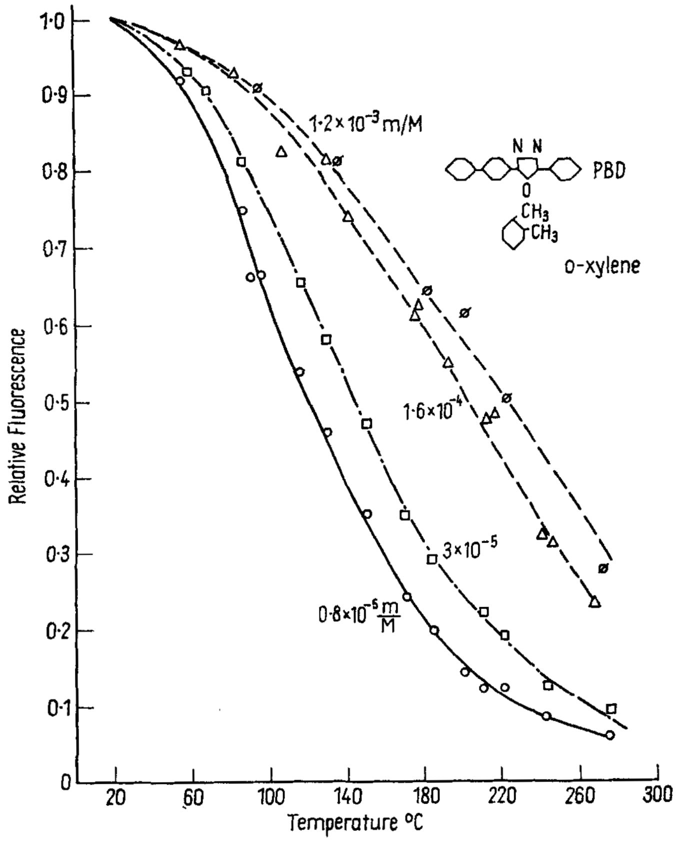

Figure 3. Fluorescence of PBD in o-Xylene at Various Temperatures - Gamma Ray Excitation (normalized)

ray excitation. One first sees a region of little or no change of fluorescence with increasing temperature and then a decrease that is relatively fast. Certainly the fluorescence decreases at a far faster rate than when the solute is directly excited. These normalized curves clearly show that temperature effects are greatest on solutions of small concentration. This occurs because the fraction of energy that is transferred is smaller at the lower concentrations.

In order to quantitatively study the energy transfer, the data must be presented in a different manner so that the variation of intensity with concentration at a given temperature can be determined. The data for

PBD in o-xylene under gamma rays is redrawn in Fig. 4. Here the maximum measured intensity at room temperature is arbitrarily given the value unity and all other intensities are measured relative to this value. A vertical cut on this set of curves gives a representation of the intensity, I, as a function of concentration, c, at a given temperature. (Only six concentrations are shown in Fig. 4, for clarity, but generally about ten concentrations are used in analyzing a system of solutions.) It is to be noted that for gamma ray excitation a correction due to density changes, because of expansion of the solution, has been applied to the

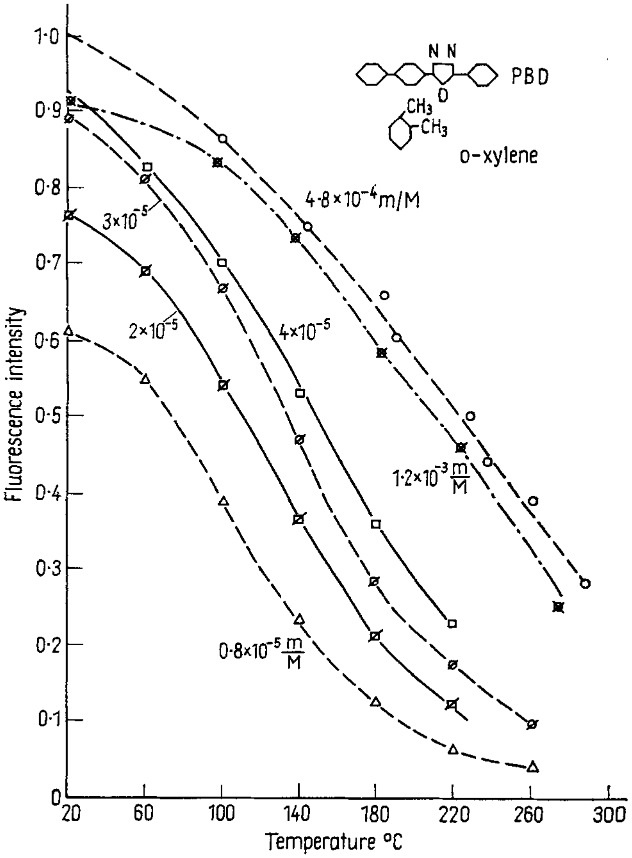

Figure 4. Fluorescence of PBD in o-Xylene at Various Temperatures. Gamma Ray Excitation.

data. This expansion results in a decrease of the gamma ray absorption in the emitting region of the apparatus. Under ultraviolet excitation this correction is not applied since all the excitation is always absorbed in the region viewed by the photomultipliers.

The results using 2650 Å excitation for PBD in o-xylene, all concentrations normalized to unity at room temperature, areshown in Fig. 5. This excitation primarily excites the solvent, because of the small concentrations of solute which are employed, but the emission is that of the solute. The results are generally of the same type as those in Fig. 3 for gamma rays, but the decrease in fluorescence is more gradual under ultraviolet. The contrast compared to 3130 Å excitation (where the solute

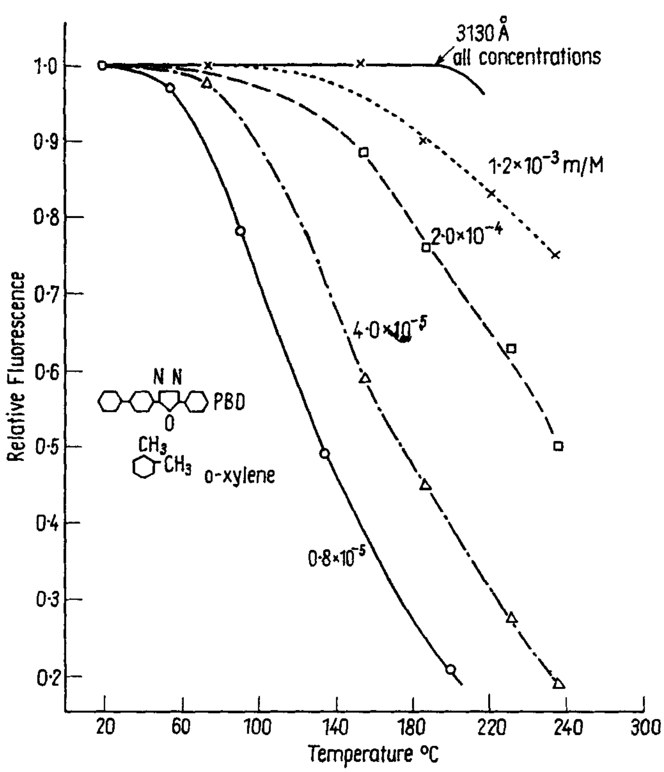

Figure 5. Fluorescence of PBD in o-Xylene at Various Temperatures—2650 Å Excitation (normalized),

absorbs) is very large, especially at small concentrations; the difference is produced mainly by the effects of temperature on the energy transfer.

Although only two solvents (o-xylene and anisole) are to be analyzed in detail with respect to energy transfer in this communication, it is worthwhile to compare the variations due to temperature of the same solute (PBD) in most of the solvents which were shown in Fig. 1. The results found for 1 g/l of PBD in these solvents under gamma ray excitation are shown in Table 1. In all the solvents, except anisole, there is a continuing decrease of fluorescence with temperature. There is a sizeable difference among the various solvents; the xylenes show the slowest variation with temperature, whereas benzene and especially cumene show the largest. The case of anisole is again quite different, it exhibits first a rise and then a fall. This is attributed to differences in the energy transfer capabilities of the monomer and excimer and will be more completely discussed below. The reason for variations among the solvents has not been ascertained. One possible reason may be excimer effects involved in some of the solvents other than anisole, but there may be other causes such as viscosity and geometrical effects.

TABLE 1 Relative Fluorescence at Different Temperatures of 1.0 g/l PBD in Various Solvents—Gamma Ray Excitation

Temperature	20°C	60°	100°	140°	180°	220°	260°
Anisole	1.0	1.14	1.08	0.95	0.75	0.53	0.33
Benzene	1.0	0.87	0.60	0.35	0.22		
Cumene	1.0	0.76	0.51	0.34	0.21	0.13	
p-Dioxane	1.0	0.80	0.63	0.49	0.37		
Toluene	1.0	0.90	0.70	0.50	0.30		
m-Xylene	1.0	0.92	0.78	0.55	0.36	0.21	0.11
o-Xylene	1.0	0.90	0.76	0.58	0.39	0.25	0.13

4. Analysis and Discussion

The analysis of the I versus c curve at a given temperature proceeds by obtaining a fit of the theoretical equation[11] with 3 determinable parameters, P, Q and R:

$$I = \frac{\dfrac{n_e}{\beta\tau_e}\, c}{\left(\dfrac{1}{\alpha\,\tau_{nt}} + c\right)\left(\dfrac{1}{\beta}\left[\dfrac{1}{\tau_e} + \dfrac{1}{\tau_i}\right] + c\right)} \equiv \frac{Pc}{(Q + c)\,(R + c)} \qquad (1)$$

to the experimental results. Of importance in this context are the following: (a) $Q \equiv \dfrac{1}{\alpha\tau_{nt}}$ which is a measure of the energy transfer; a large Q signifies a small efficiency of transfer. The value of Q gives the concentration of solute at which half of the energy is transferred. (b) $\dfrac{P}{R} \equiv \dfrac{n_e}{(1 + \tau_e/\tau_i)}$ is a measure of the solute efficiency under energy transfer conditions in the absence of selfquenching. The factor n_e represents the number of excited solvent molecules which are available for transfer. (This, under high energy radiation, may be less than the number directly energized.) The ratio τ_e/τ_i is the ratio of the radiative time constant of the solute and the time for "internal" non-radiative transitions in the solute and in any case is determined mainly by the solute.

α	is a constant relating the transfer probability, from solvent to solute, to solute concentration.
τ_{nt}	is the lifetime associated with non-transfer processes of the solvent.
β	is a constant relating self quenching probability to solute concentration.

Table 2 gives the calculated parameters for PBD in o-xylene under both gamma ray excitation and UV excitation. The outstanding point to be noted is the large increase in Q, a factor of more than 6 for 180°K change ($>$ 20 for a 300°K change not shown in these tables); the change in Q is not linear. The factor R remains effectively unchanged in these experiments up to 350°K. Since the parameter R depends almost entirely on solute factors, the constancy indicates that there is little or no change

TABLE 2 Parameters for PBD in o-Xylene — $\frac{\mathrm{m}}{\mathrm{M}}$

Gamma Ray Excitation				
T°C	*P*	*Q*	*R*	*P/R*
20°	6.6×10^{-2}	0.69×10^{-5}	6.1×10^{-2}	1.1
60°	6.7×10^{-2}	0.81×10^{-5}	6.5×10^{-2}	1.0
100°	5.9×10^{-2}	1.3×10^{-5}	6.1×10^{-2}	0.97
140°	5.0×10^{-2}	2.4×10^{-5}	5.7×10^{-2}	0.88
180°	4.1×10^{-2}	4.4×10^{-5}	5.5×10^{-2}	0.75
Ultraviolet Excitation				
20°	6.6×10^{-2}	0.69×10^{-5}	6.1×10^{-2}	1.1
100°	6.8×10^{-2}	1.18×10^{-5}	6.5×10^{-2}	1.05
140°	6.7×10^{-2}	2.2×10^{-5}	6.5×10^{-2}	1.03
180°	6.2×10^{-2}	4.1×10^{-5}	6.3×10^{-2}	0.99

in the basic solute emission mechanism. This is in agreement with the result of little change in fluorescence when ultraviolet radiation which directly excites the solute is used. The factor P/R does, however, show a gradual decrease when the temperature is raised. (Less precise results based on a smaller number of concentrations previously reported[1] indicated that P/R varied to a smaller extent than the present results.) When these parameters are compared with those using ultraviolet excitation, a great similarity is found; the magnitudes of Q are about the same, and R is also constant. P/R does show a decrease but to a smaller extent (it is nearly constant) than under gamma rays. The decrease in P/R is most likely due to a change in n_e. The greater change of P/R under gamma ray excitation is associated with the involvement of higher levels of excitation (or ionization) in the eventual availability of the transferring molecules.

Experiments similar to those in o-xylene were carried out for PBD in anisole and the normalized results are gathered in Figs. 6 and 7, while the calculated parameters are shown in Table 3. It is clearly seen that in anisole temperature has a decidedly different effect on the fluorescence under energy transfer conditions than in o-xylene. At small concentrations the difference is particularly marked since in o-xylene one has the steepest fall-off of fluorescence, whereas in anisole there is the sharpest rise. It is to be noted that under 3130Å excitation in Fig. 7 (exciting the

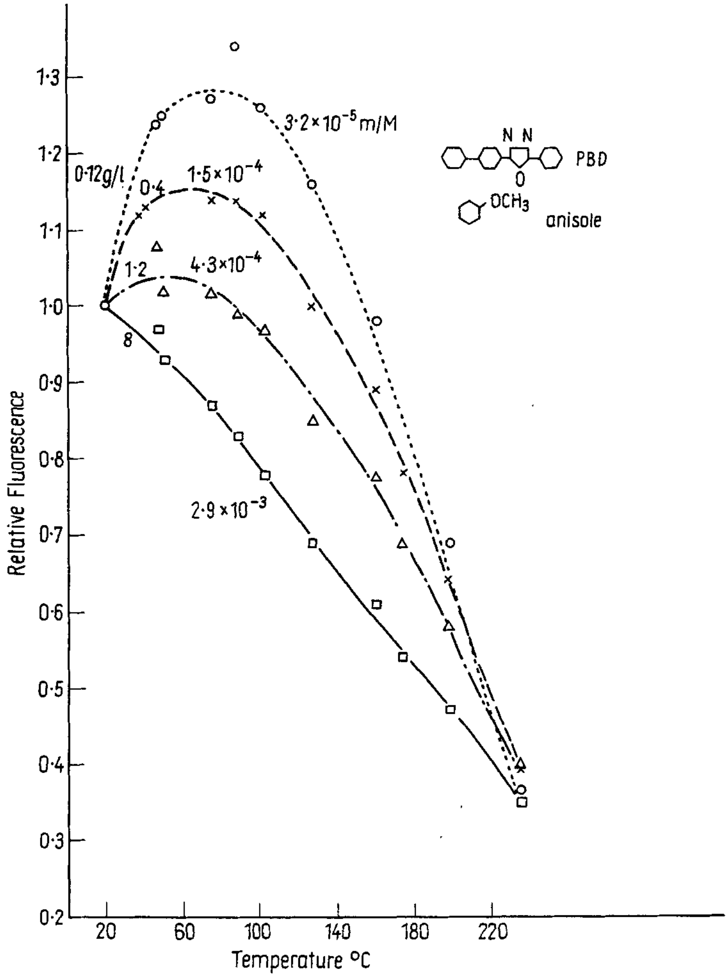

Figure 6. Fluorescence of PBD in Anisole at Various Temperatures. Gamma Ray Excitation (normalized).

solute directly), the fluorescence scarcely changes, which is similar to the behavior in o-xylene. Under 2750 Å excitation at the highest concentration (2.9×10^{-3} m/M), the fluorescence is almost unchanged for the range of temperatures. This is interpreted as occurring because the energy transfer from the monomer component is essentially complete at these high solute concentrations. At lower concentrations there is an

TABLE 3 Parameters for PBD in Anisole — $\frac{m}{M}$

T°C	*P*	*Q*	*R*	*P/R*
Gamma Ray Excitation				
20°	6.0×10^{-2}	1.5×10^{-5}	5.4×10^{-2}	1.1
60°	5.3×10^{-2}	0.82×10^{-5}	5.4×10^{-2}	1.0
100°	4.5×10^{-2}	0.47×10^{-5}	5.4×10^{-2}	0.83
140°	3.8×10^{-2}	0.43×10^{-5}	5.4×10^{-2}	0.71
180°	3.0×10^{-2}	0.50×10^{-5}	5.4×10^{-2}	0.57
220°	2.3×10^{-2}	0.86×10^{-5}	5.4×10^{-2}	0.43
Ultraviolet Light Excitation				
20°	6.6×10^{-2}	$.86 \times 10^{-5}$	5.1×10^{-2}	1.22
60°	6.6×10^{-2}	$.50 \times 10^{-5}$	5.1×10^{-2}	1.23
100°	6.6×10^{-2}	$.47 \times 10^{-5}$	5.1×10^{-2}	1.22
140°	6.4×10^{-2}	$.50 \times 10^{-5}$	5.1×10^{-2}	1.19
180°	6.3×10^{-2}	$.64 \times 10^{-5}$	5.1×10^{-2}	1.17

enhanced fluorescence. This comes about because of the relative decrease in excimer population and the better transfer from the monomer. These ideas are borne out by the variation in *Q* parameter in Table 3; it first decreases, indicating a better transfer as the temperature is raised and finally increases again at the highest temperature because transfer from the monomer is reduced at high temperatures as in other solvents. The gamma ray results shown in Fig. 6 have a similar enhancement (though somewhat smaller) with temperature at low concentrations, but the high concentration fluorescence decreases markedly, even though energy transfer is presumably nearly complete. This large difference between gamma ray excitation and UV excitation at high concentrations is a very definite indication that higher levels are involved in the process.

Values for the parameter *R* for anisole are also found to be constant and not very different from those in o-xylene. The room temperature value of *Q* is more than a factor of two greater than for o-xylene; it represents a composite of the contributions from monomer and dimer. However, at high temperatures the *Q* for anisole is well below that of o-xylene at the some temperature; at 450°K the anisole is a more efficient transferring agent by a factor of 9 under gamma ray excitation. This may be practical importance if high temperatures are required in high energy fluorescence work. At the same time, the parameter *P* is diminished by a factor of 2 upon raising the temperature to 450°K under gamma

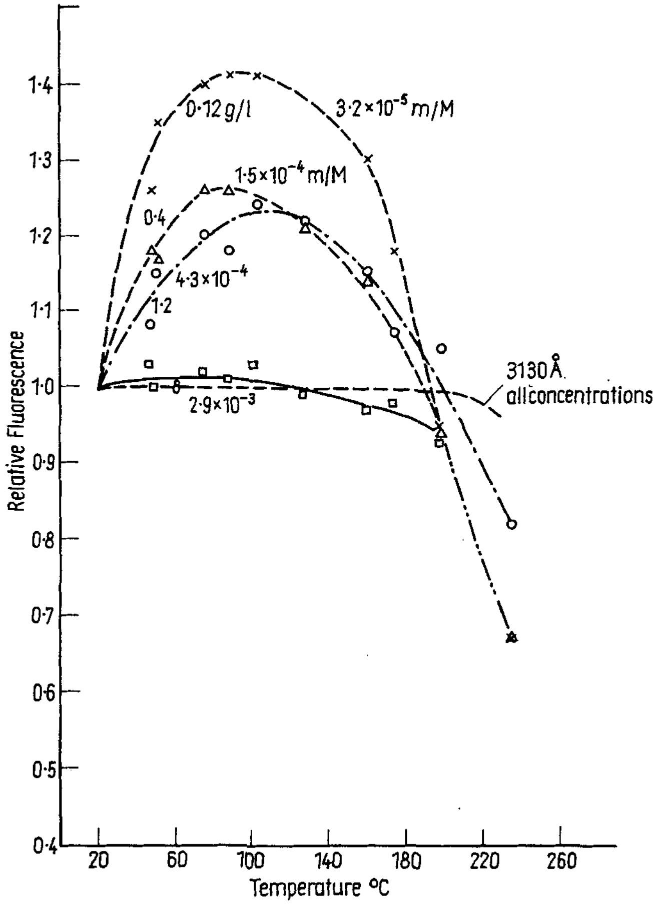

Figure 7. Fluorescence of PBD in Anisole at Various Temperatures —2750 Å Excitation (normalized).

ray excitation. Under UV excitation the type of Q variation is not greatly different from that under gamma rays; however, the P/R variation is very much smaller under the ultraviolet excitation. The latter provides one of the most marked indications of the role of higher levels. For aid in clarity, the variations with temperature for Q and P/R using both solvents are shown for gamma ray excitation in Fig. 8.

It was shown in reference 1 that the data for parameter Q for PBD in o-xylene could be well represented by an expression of the form

$Q = Q_{RT}Ae^{BT/\eta_v}$ where Q_{RT} is the room temperature value of Q and η_v is the viscosity of the solvent and A and B are constants. The more extended data obtained here and the values obtained using light excitation are in accord with such an expression. These results containing the viscosity indicate that the energy transfer does have some connection with motion in the solution, but it does not necessarily mean that diffusion of the transferring molecule is taking place to such a degree that it is the dominant factor in transfer. The vibration of the excited solvent molecule and its ability to interact with nearby molecules may be dependent on the viscosity.[3] A reduction in viscosity at higher temperature would then lead to a greater interaction and a reduced excitation lifetime of the solvent.

According to the theory used in obtaining equation (1) above, it follows that the energy transfer parameter Q and the relative efficiency of the solvent η_{sv} (Figs. 1 and 2) are related[1] by:

$$Q\eta_{sv} = \frac{1}{\alpha\tau_R} \tag{2}$$

where $\frac{1}{\tau_R}$ is the radiation probability of a solvent molecule and α is a measure of the cross-section for transfer from solvent to solute. It seems reasonable to assume that the value of τ_R does not change very much with temperature, since the emission of a substance at high temperature, such as PBD, is not changed very much, and as far as is known there is no report of significant change of absorption spectrum with temperature. If this is a correct assumption, one is then lead to $Q\eta_{sv} = \text{constant}\,\alpha^{-1}$.

One of the most significant results of this work is that $Q\eta_{sv}$ is found to be almost a constant as a function of temperature[1] for a number of solutes. (PBD, α-NPO and p-terphenyl were investigated in o-xylene under gamma rays.) The more complete results here, shown in Table 4 on PBD and p-terphenyl for gamma ray excitation, are in good accord with the earlier results and moreover the value under UV excitation is more constant. A constant $Q\eta_{sv}$ then implies, using the above considerations, that the value of α (the transfer coefficient) is also a constant as a function of temperature; even though the average distance between molecules is larger at higher temperatures. Furthermore, the constancy of $Q\eta_{sv}$ then directly indicates that the changes in energy transfer parameter are due almost entirely to the variation of solvent lifetime as

TABLE 4 $Q\eta_{sv}$ for PBD and p-Terphenyl in o-Xylene and Anisole — g/l

	PBD			
	o-Xylene		Anisole	
T°C	γ-rays	U.V.	γ-rays	U.V.
20°	0.17	0.17	0.42	0.24
60°	0.16	—	0.26	0.17
100°	0.12	0.14	0.13	0.19
140°	0.12	0.15	0.098	0.18
180°	0.11	0.17	0.087	0.19
220°	—	—	0.077	—
	p-Terphenyl			
20°	0.12		0.60	
60°	0.11 (80°)		0.45	
100°	0.10 (120°)		0.30	
140°	0.09 (150°)		0.25	
180°	0.10		0.19	

reflected by its relative fluorescence. This seems to be due mostly to changes in interaction with neighboring molecules rather than a change in emission probability. It thus appears that the energy transfer variations are not primarily caused by changes in velocity and distance of travel unless these effects directly counteract each other throughout the temperature range.

In Table 4 the $Q\eta_{sv}$ results using anisole are also shown. In this case one expects more complicated results because of the large influence of excimers on the results. It is not necessarily the case that variation in fluorescence of the solvent is a direct measure of the change in solvent lifetime since the relative fluorescence depends greatly on the different efficiencies of monomer and excimer emission and their relative populations. The parameter Q may have quite a different dependence on the relative amounts of these two species. Nevertheless, the results in Table 3 and in Fig. 1 indicate that qualitatively as η_{sv} goes down, Q goes up and vice versa. If one could correctly "subtract" the dimer effect and study only the monomer, one might expect a behavior similar to other solvents. Under gamma rays manisole one sees a strong decrease of $Q\eta_{sv}$ in anisole solutions when using either PBD or p-terphenyl. This

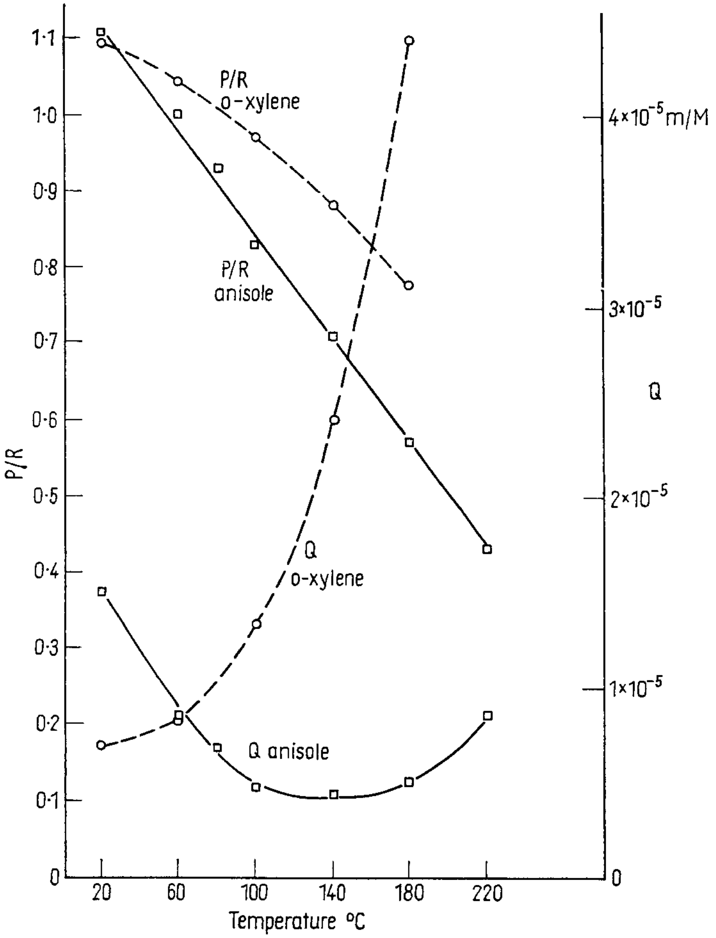

Figure 8. Parameters for PBD in o-Xylene and in Anisole at Various Temperatures —Gamma Ray Excitation.

shows that the dependence of Q and η_{sv} on dimeric populations is different. Under ultraviolet excitation the situation appears quite different. Here $Q\eta_{sv}$ is nearly constant, especially for PBD. The difference in results between the two excitations is quite large and may also be associated with higher excitation levels, although the use of Eq. (1) without modification for the case with two transferring species present may be questionable. Further investigation is required.

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