STUDY OF ENERGY TRANSFER BY QUENCHING EXPERIMENTS*

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INTRODUCTION

Four possible processes have been described by which excitation energy produced in the bulk of liquid or solid material can reach a fluorescent solute. These are:

1. Direct energy transfer by a single jump from the excited bulk molecule to a solute molecule over several molecular diameters (Forster mechanism).

2. Migration of excitation energy from bulk molecule to neighboring bulk molecule until the excitation energy comes close enough to a solute molecule for transfer to occur very efficiently. Thus, the final step of process 2 is transfer from the solvent to the solute but this time over considerably smaller distances than process 1.

3. Actual movement of the excited bulk molecule into the neighborhood of the solute molecule (material diffusion) followed by transfer. This diffusion process cannot occur in a rigid medium.

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4. Energy transfer via radiation wherein the bulk molecule emits radiation which is absorbed by the solute which emits in turn with its characteristic spectrum.

All four processes were described in earlier papers (1). Process 4 is found to be insignificant in many cases of interest and especially in liquid and rigid solutions of a single solute in a single solvent. When two emitting solutes are present, a shift in emitted wavelength may occur due to radiation transfer. This wavelength shift was described and interpreted by Kallmann and Furst in 1951 (1,2). However, processes 1, 2, and 3 seem to contribute to energy transfer in varying degrees, depending upon the type of bulk material (for example, whether it is a liquid or a plastic) and also to a certain extent upon the solute (3). It is stated by Birks in a recent paper (4) that we have, in general, abandoned process 3 in favor of process 2; this is not the case. There is evidence that all three transfer processes occur. The purpose of the investigation described herein was to discriminate between the effects of the different processes and to find in which cases each is most significant.

This was carried out by studying the quenching of the bulk material and comparing with processes in which the energy is transferred from the bulk to the fluorescent solute. The significant difference between quenching and fluorescence lies in the existence of an energy state in the fluor which can take over the excitation energy of the bulk; this is not the case for most quenching molecules; they only produce a dissipation of the energy. Process 1 is, therefore, ruled out in the quenching processes discussed here. Processes 2 and 3, however, can be effective for quenching in liquids. Quenching will take place when the excitation energy comes close enough to a quencher molecule for dissipation to occur. In plastics, this can be brought about only by process 2. Otherwise it could occur only when an excited bulk molecule happens to be created near a quencher molecule; this is a rare occurrence at low quencher concentrations.

A measure of the occurrence of 2 can then be obtained by investigating quenching at low quencher concentrations in a rigid plastic. On the other hand, in a dilute liquid solution process 3 is primarily responsible for solute quenching since there is little migration of energy from solute molecule to solute molecule because of their large separation. Thus, the extent of solute quenching in a liquid indicates the degree to which process 3 takes place in the solute. A quantitative comparison between these processes would be possible only if the effective cross sections for these final steps (dissipation or transfer) were accurately known; this is not the case. It may be conjectured, however, that final step in energy transfer to a fluorescent solute should have a larger cross section than the final step in a quenching process because transfer is a resonance process. Transfer should thus be possible over greater distances than quenching in which no resonance is involved. However, this does not appear to occur since it was observed rather early in liquid scintillator work that efficiencies of energy transfer to a fluorescent solute are in many cases of the same order of magnitude as the efficiency of bulk quenching. This is clearly seen by examining the concentration at which half of the fluorescence transfer occurs (half value concentration); it is not much smaller than the half value of the quenching concentration. These results indicate that migration and/or diffusion contribute significantly in both cases. In order to obtain more information about these processes, quenching was investigated in some detail for three different cases.

Equation 1 gives the amount of quenching as a function of the quencher (degrader) concentration c_D and solute (acceptor) concentration c_A:

$$\frac{I_o}{I} - 1 = \tau_B C_D \delta \frac{N_A(\infty) - N_A(C_A)}{N_A(\infty)} \qquad \text{(Eq. 1)}$$

In this equation, I and I_o are respectively the intensities of the fluorescence with and without quencher added to the solution; $N_A(\infty)$ is the number of excited fluorescent solute molecules energized by transfer present at infinite solute concentration, $N_A(C_A)$ is the number at concentration c_A, both in the absence of quencher. Both $N_A(\infty)$ and $N_A(C_A)$ are proportional to the observed light emission extrapolated to zero concentration quenching. In the basic equation for high energy induced fluorescence intensity as a function of solute concentration c_A,

$$I = \frac{P C_A}{(Q + C_A)(R + C_A)}$$

the N's are proportional to $\frac{C_A}{Q + C_A}$. δ is the proportionality factor for processes 2 and/or 3, which lead to quenching; and $\frac{1}{\tau_B}$ is the probability of the spontaneous decay of an excited bulk molecule. In previous notation, $\frac{N_A(\infty) - N_A(C_A)}{N_A(\infty)}$ becomes $\frac{Q}{Q + C_A}$, where Q is the concentration at which half the energy is transferred to the solute in the absence of quencher. In essentially the latter form, Eq. 1 was used by Burton and Lipsky to determine the quenching of the bulk material by various quenching agents (5).

According to Eq. 1 as c_A increases, the quenching becomes small. Physically, this can be interpreted as coming about because more and more of the energy is transferred to the solute before quenching can occur. If the solute concentration is kept constant while c_D is varied, the quencher expression on the left of Eq. 1 should bear a linear relationship to the quencher concentration c_D. This behavior was found by Burton and Lipsky and was confirmed in our experiments.

In these experiments, the quenching of the bulk material is determined from measurements of the fluorescence while exciting the bulk material either by high energy or by light. Equation 1 does not take into account that energy in the solute molecule may also be quenched by the quenching agent. In many cases, this can be neglected because the quenching of the solute has been found to be considerably smaller than the quenching of the bulk material (7). This point will be discussed further in Section 3. In the experiments herein reported, quenching of the solute by the quenching agent was separately determined by exciting the solute directly by light. From these measurements, the observed light emission can be extrapolated to zero solute quenching by the quenching agent. Equation 1 refers to intensities corrected to zero solute quenching.

Analysis of fluorescence and quenching by Eq. 1 reveals several noteworthy effects: First, as mentioned above, quenching should become very small at large solute concentrations c_A; this is not always found (see Section 2). Second, it has been observed that the quenching of solute molecules by a quencher is always considerably smaller than the quenching of the usual bulk molecules used in scintillation work. Xylene or benzene, for example, is quenched much more than 9,10-diphenylanthracene, and the same is true for naphthalene molecules when used as bulk material. It was conjectured (6) that this may be due to the effectiveness of processes 2 and/or 3 in quenching the bulk molecules (solvent), whereas quenching of the solute molecules occurs only via process 3. In order to clarify the situation, the efficiency with which the bulk material is quenched was studied as a function of its concentration when dispersed in a poorly transferring medium. Previous experiments over a small concentration range (6) exhibited only a small effect of concentration on solvent quenching. Experiments over wider concentration ranges show that there is an effect, but it is smaller than expected (see Section 3).

Third, there is a difference between quenching in liquid and rigid (plastic) material. In a rigid medium, as pointed out above, only process 2 can bring about quenching at low quencher concentrations. The results of our experiments show, however, that quenching may occur under certain circumstances as strongly in rigid as in liquid media; this is a strong indication for the occurrence of process 2 in rigid media (see Section 4).

DEPENDENCE OF SOLVENT QUENCHING UPON SOLUTE CONCENTRATION

As pointed out, in some instances solvent quenching does not become very small at high solute concentrations, although this is predicted from Eq. 1. Figure 1 shows the quenching under gamma ray excitation of 1-methylnaphthalene by carbontetrachloride using 9,10-diphenylanthracene as the light-emitting solute at various carbontetrachloride and solute concentrations. Figure 2 gives the results of similar experiments using *p*-xylene with fluoranthene as fluorescent solute. Both figures show that small quencher concentrations are sufficient to produce strong quenching at low solute concentrations, whereas quenching almost disappears at high solute and low quencher concentrations. Even large quencher concentrations are relatively ineffective at high solute concentrations. These results are in general agreement with Eq. 1. Cases which deviate from predicted behavior are shown in Figs. 3 and 4. These describe experiments similar to those above and were performed in *p*-xylene with *m*-terphenyl and pyrene, respectively, as fluorescent solutes. These solutes were selected because of their high solubility so that the relationship between quenching and solute concentration could be studied up to high concentrations. Figure 3 shows that at *m*-terphenyl concentrations as high as 200 g/1 (0.9 M), 5 g/1 carbontetrachloride (corresponding to only 0.03 M) quenches considerably. An

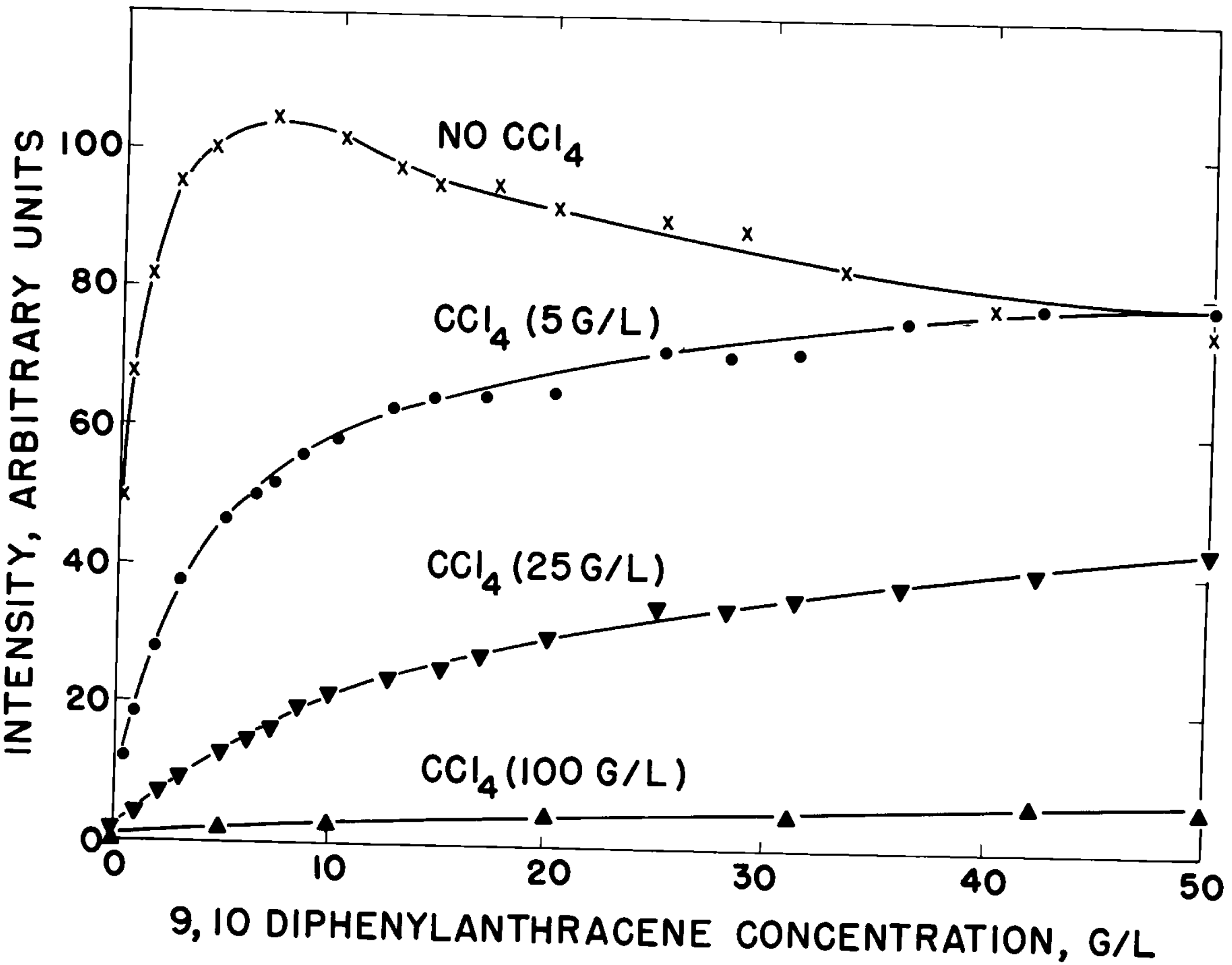

Fig. 1. Effect of CCl_4 on gamma ray induced fluorescence of 9,10-diphenylanthracene in 1-methylnaphthalene.

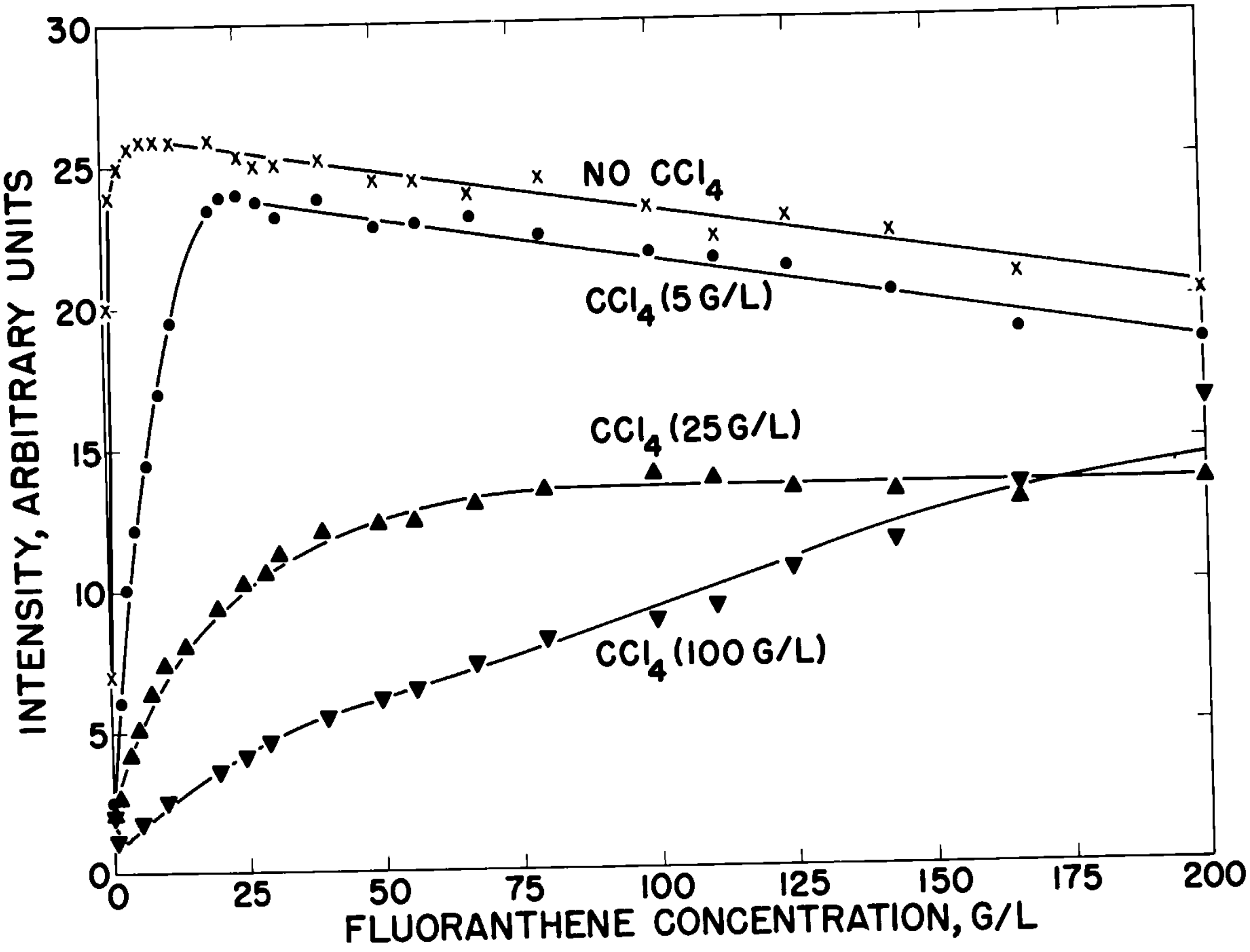

Fig. 2. Effect of CCl_4 on gamma ray induced fluorescence of fluoranthene in p-xylene.

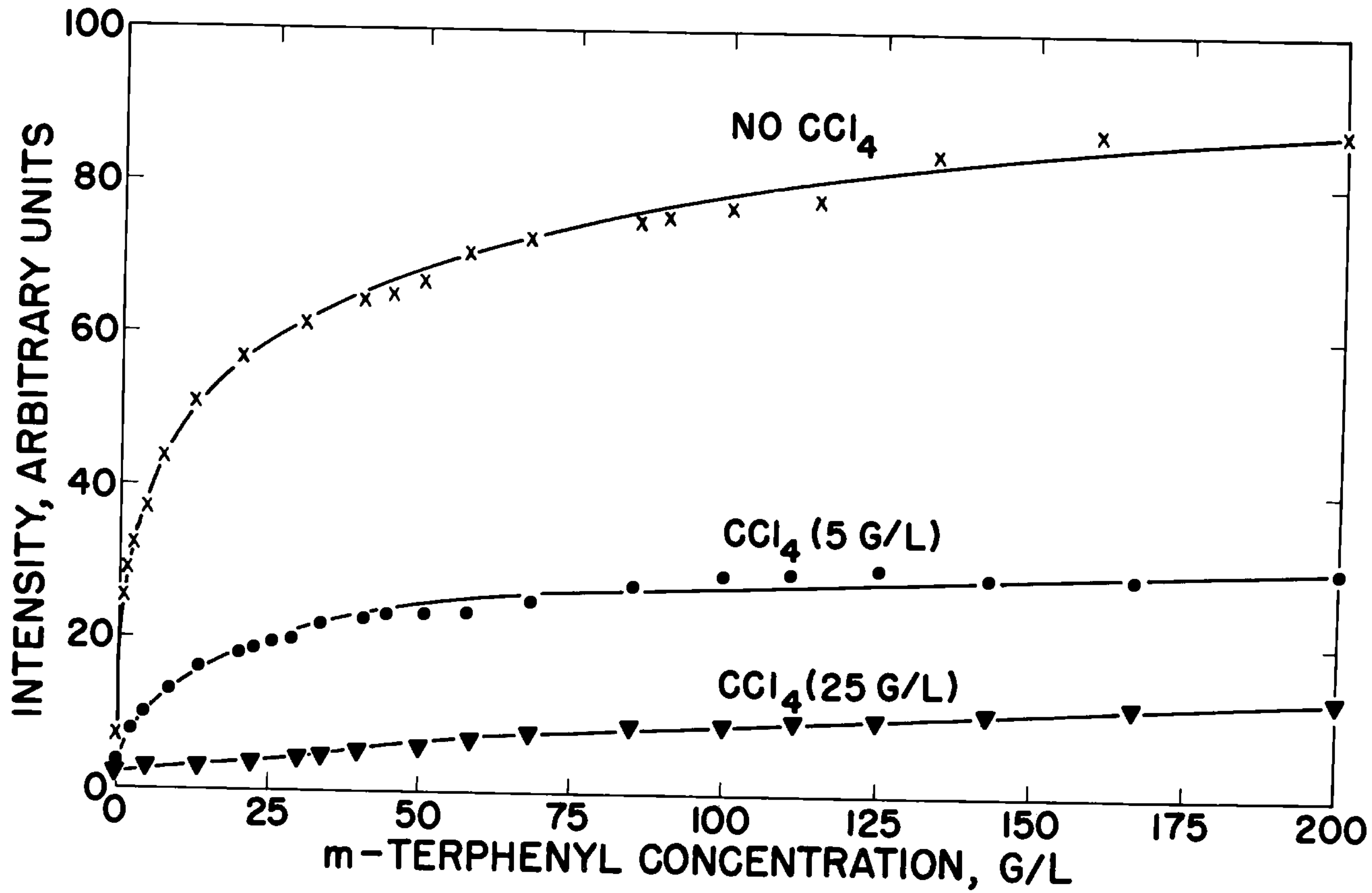

Fig. 3. Effect of CCl_4 on gamma ray induced fluorescence of m-terphenyl in p-xylene.

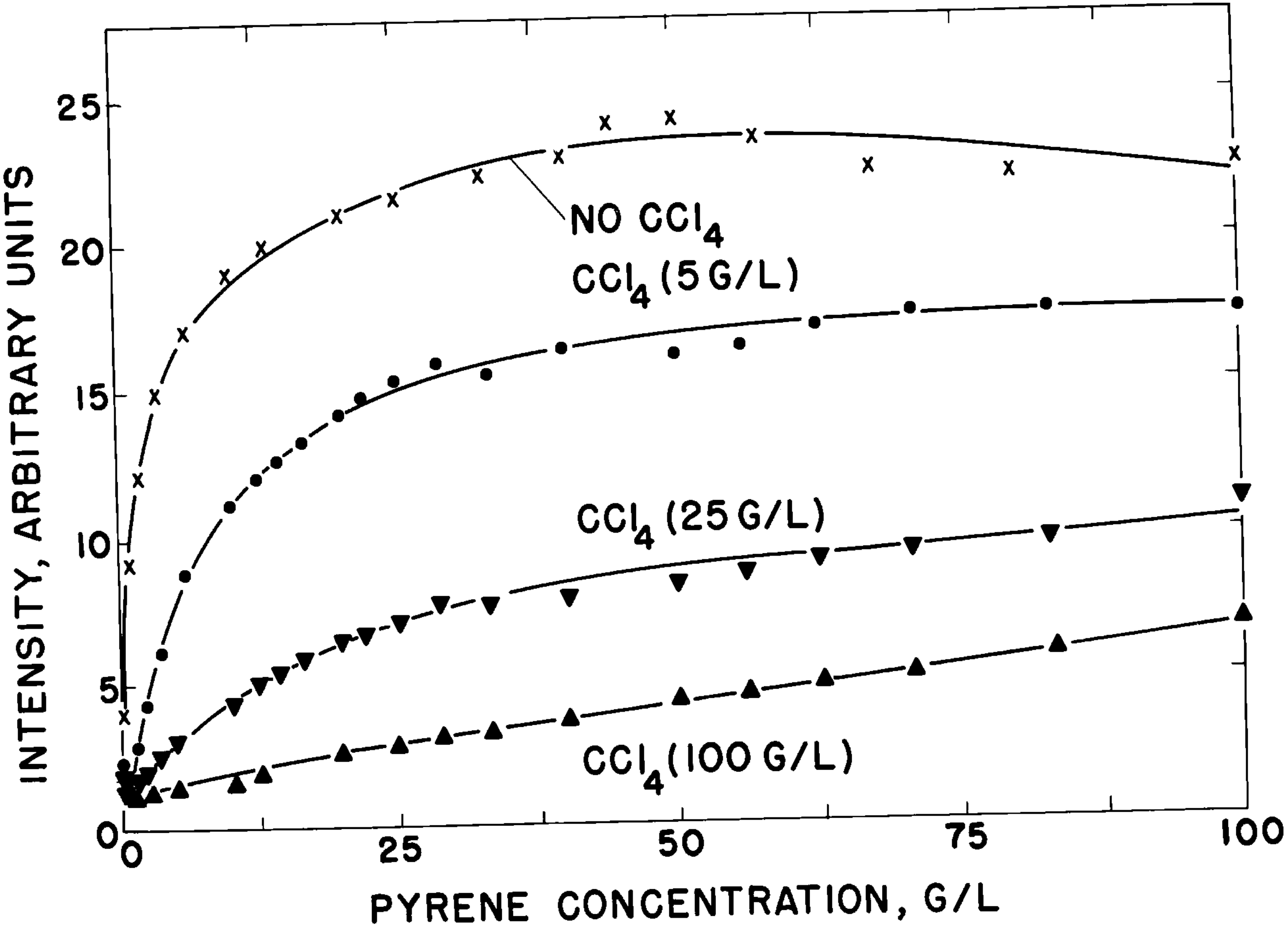

Fig. 4. Effect of CCl_4 on gamma ray induced fluorescence of pyrene in p-xylene.

important feature of the results in Figs. 3 and 4 is that quenching decreases only slightly when the solute concentration is increased by a factor of almost 10; whereas, according to Eq. 1, the quenching should be much more reduced. A similar result is observed for pyrene as solute. Although the decrease in quenching at high solute concentration is, in this case, quite noticeable, it is still considerably smaller than expected from Eq. 1. The quenching is reduced only slightly when the solute concentration is increased by a factor of 4. For example, at a pyrene concentration of 25 g/l, the quenching factor $\frac{I_o}{I}$ -1 is 2.8 for 25 g/l carbontetrachloride, whereas the quenching at 100 g/l pyrene by the same concentration of carbontetrachloride is still more than 2. According to Eq. 1, a decrease in quenching by a factor of almost 4 is expected for this increase in solute concentration; whereas, the measurements show that $\frac{I_o}{I}$ - 1 decreases only from 1.8 to 1.2.

The explanation for this deviation from the predicted behavior has not yet been ascertained. There are several possibilities which could account for these results. Both m-terphenyl and pyrene are solutes which behave in a somewhat unusual manner with respect to energy transfer; they have large Q values (which indicates smaller transfer efficiencies) compared to other efficient scintillating solutes which have so far been investigated. The paper by Wirth at this meeting indicates that there may be other such substances (8). But this is not enough to explain the results shown in Figs. 3 and 4. It may be that those Q values do not measure the energy transfer in these cases. For example, it may be that at higher solute concentrations, significant self-absorption of the emitted light takes place so that the true energy transfer curve for the solute is quite different from the observed curve. In this circumstance, the Q values determined from the energy transfer curve would be too small and the correct Q values would be larger than those deduced from the curves. In the absence of this hypothetical absorption, the fluorescent light would be considerably greater at high solute concentration. This possible explanation of deviations will be checked by absorption measurements. It would imply that the true Q values of these substances are quite large compared to those of common effective scintillators and certainly larger than those determined from the fluorescence versus concentration curves. Another possible explanation is the formation of m-terphenyl aggregates at high concentrations. The energy traversing the solvent would not reach one of these aggregates with much greater probability than it would an isolated solute molecule, since the cross section of the aggregate increases relatively slowly with the number of molecules making up the aggregate. Therefore, the effective concentration for energy transfer would be much smaller than the actual concentration. A further lead may come from an investigation of decay time constants of these substances in solution as a function of concentration.

COMPARISON BETWEEN QUENCHING OF SOLUTE AND BULK MOLECULES

There is generally a large difference in the extent to which solute and bulk material molecules are quenched in efficient scintillators. This means that the same molecule (e.g., 1-methylnaphthalene) is quenched differently when used as solvent or solute. This difference in a liquid scintillator may be due at least partially to the occurrence of both transfer processes 2 and 3. Quenching of the bulk molecule thus can occur via both processes. Solute quenching, however, can take place only via material diffusion process 3 because the solute molecules are too far apart for migration.

In solutions in which process 2 is as effective or more effective than process 3, one would expect that quenching of bulk molecules decreases when they are diluted by an inactive medium. (These molecules will be called bulk molecules even after this dilution, although the inactive medium may be the major constituent.) In order to test this hypothesis, solutions using o-xylene or 1-methylnaphthalene as bulk material, α-naphthylphenyloxazole as fluorescent solute, n-butylphosphate as the diluting inactive substance, and carbontetrachloride or α,α,α,α',α',α'-hexachloro-p-xylene as quenchers were investigated under gamma ray excitation. The concentration of fluorescent solute was kept constant during a run but various amounts of xylene or 1-methylnaphthalene, respectively, were present. The quenching of the fluorescent solute is small compared to the quenching of o-xylene or 1-methylnaphthalene, so that the quenching of the solution is essentially due to solvent quenching. Preliminary experiments showed that quenching does indeed decrease with greater dilution of the bulk material, but to a smaller degree than expected (6). The results over a wide range of concentration are given in Figs. 5 and 6.

The curves of Figs. 5 and 6 are linear, which is in accordance with Eq. 1. The uppermost curve in Fig. 5 represents the

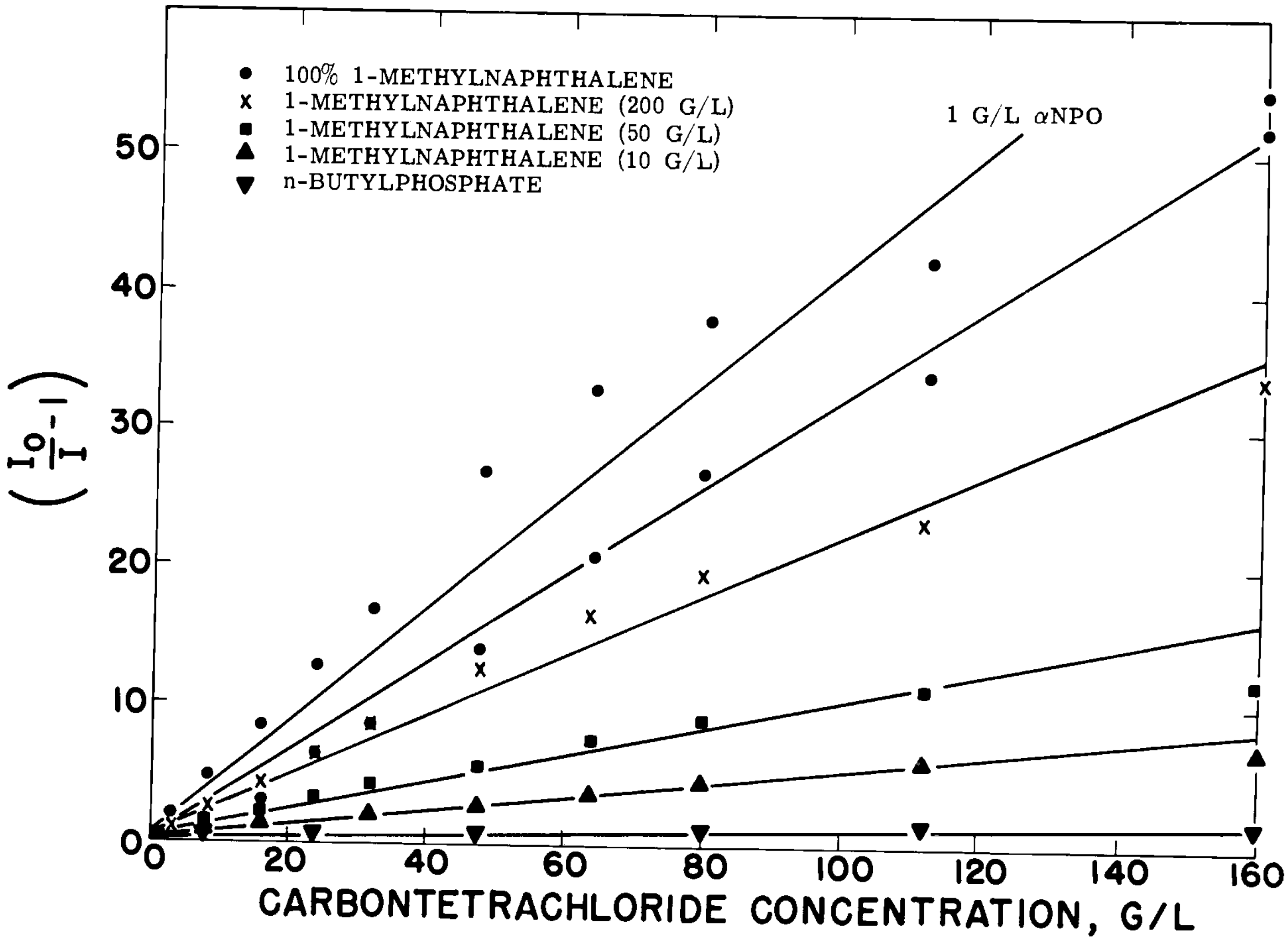

Fig. 5. Effect of CCl_4 on gamma ray induced fluorescence of 3 g/l of α-naphthylphenyloxazole in combinations of n-butylphosphate and 1-methylnaphthalene.

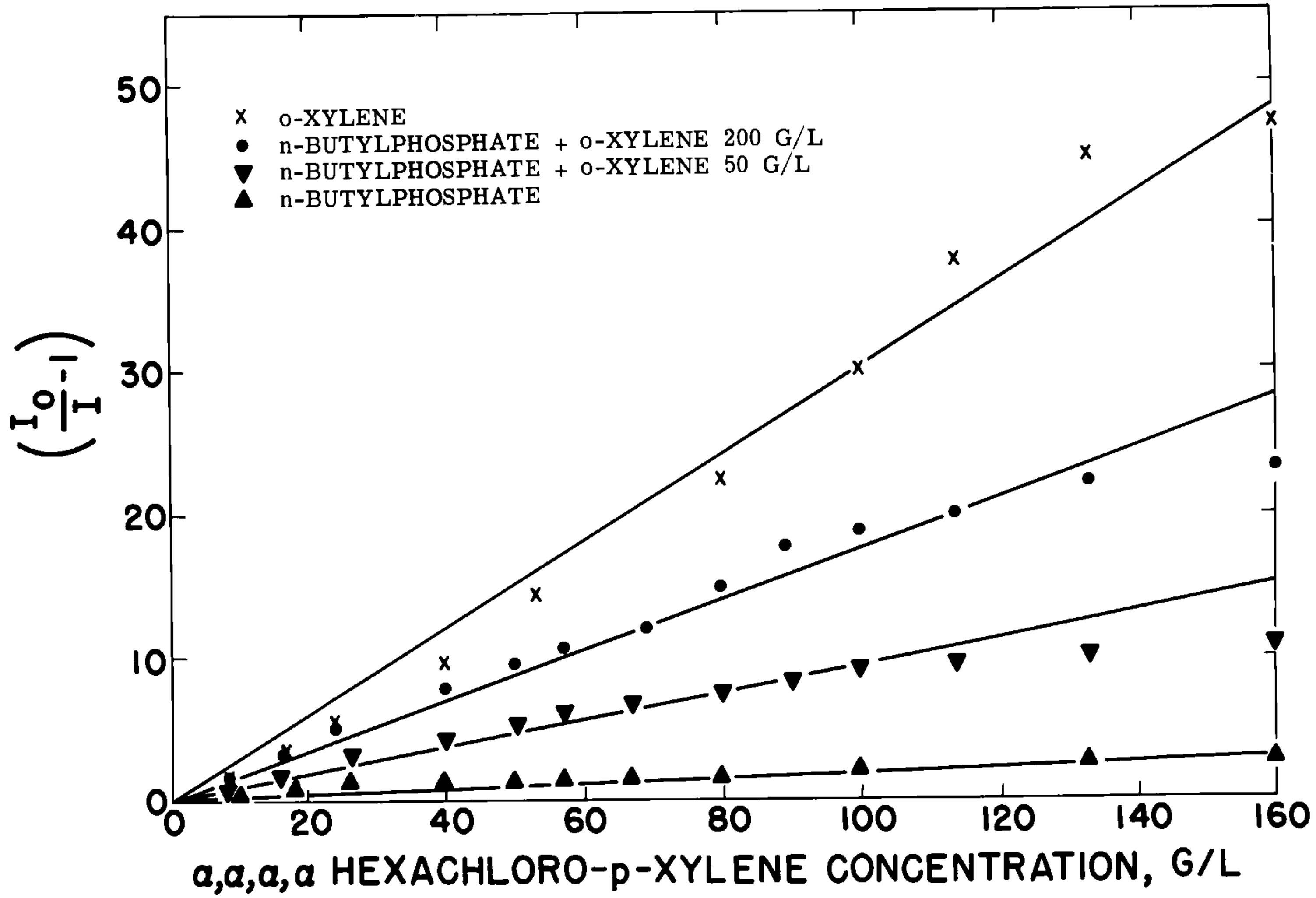

Fig. 6. Effect of α,α,α,α-hexachloro-p-xylene on gamma ray induced fluorescence of 3 g/l of α-naphthylphenyloxazole in combinations of n-butylphosphate and o-xylene.

quenching in the undiluted solvents, whereas the lowest curves give the quenching when only the diluent (n-butylphosphate) is present. Quenching in solutions made in n-butylphosphate alone is seen to be small even at the largest quencher concentration used, and even part of this is due to solute quenching. The other curves in Fig. 5 show the quenching for various degrees of dilution. At 200 g/l o-xylene, a dilution to about 20 per cent, the quenching has decreased by a factor of more than 2; and at 50 g/l o-xylene, a dilution to about 5 per cent, the quenching has decreased by a factor of more than 4 compared with no dilution. Figure 6 describes similar experiments for 1-methylnaphthalene. The uppermost curve is for 1 g/l of α-naphthylphenyloxazole; all the other measurements are for solute concentrations of 3 g/l. This group of curves also shows a decrease in solvent quenching with increasing dilution. The two upper curves show that the influence of solute concentration is smaller than expected from Eq. 1. Figure 7 presents the light emission curves of various dilutions of 1-methylnaphthalene in n-butylphosphate as a function of the solute concentration in the absence of added quencher. This lowest curve shows that the light emission in n-butylphosphate alone is quite small. In solutions containing only 10 g/l of methylnaphthalene, the emissionis considerably greater and most of the light emission is due to energy transfer via methylnaphthalene. Thus only a small amount is transferred directly from butylphosphate to the fluorescent solute despite its greater abundance.

These experiments clearly show the decrease in quenching of the bulk molecule with increasing dilution. This behavior can be interpreted in the following way. In methylnaphthalene or o-xylene alone, the excitation energy reaches the neighborhood of the quencher mainly by migration, and this process seems to be considerably more effective than the material diffusion. Previously (6) the smaller decrease of quenching than expected between o-xylene and 30 per cent o-xylene was interpreted to mean that process 3 is of considerable importance; the considerable decrease in quenching observed at still greater dilutions seems to require the interpretation given here. However, the decrease of quenching is certainly much smaller than that calculated, since quenching should be approximately proportional to (H is bulk molecule concentration and n may have the values 2, 4, 8....); n depends upon the mechanism for the exchange of energy between bulk material molecules.

The reason that quenching is smaller than calculated may be understood from Eq. 1. The factor δ is a measure of the effectiveness of migration and/or diffusion. If migration is more important than diffusion in the undiluted solvent, δ should

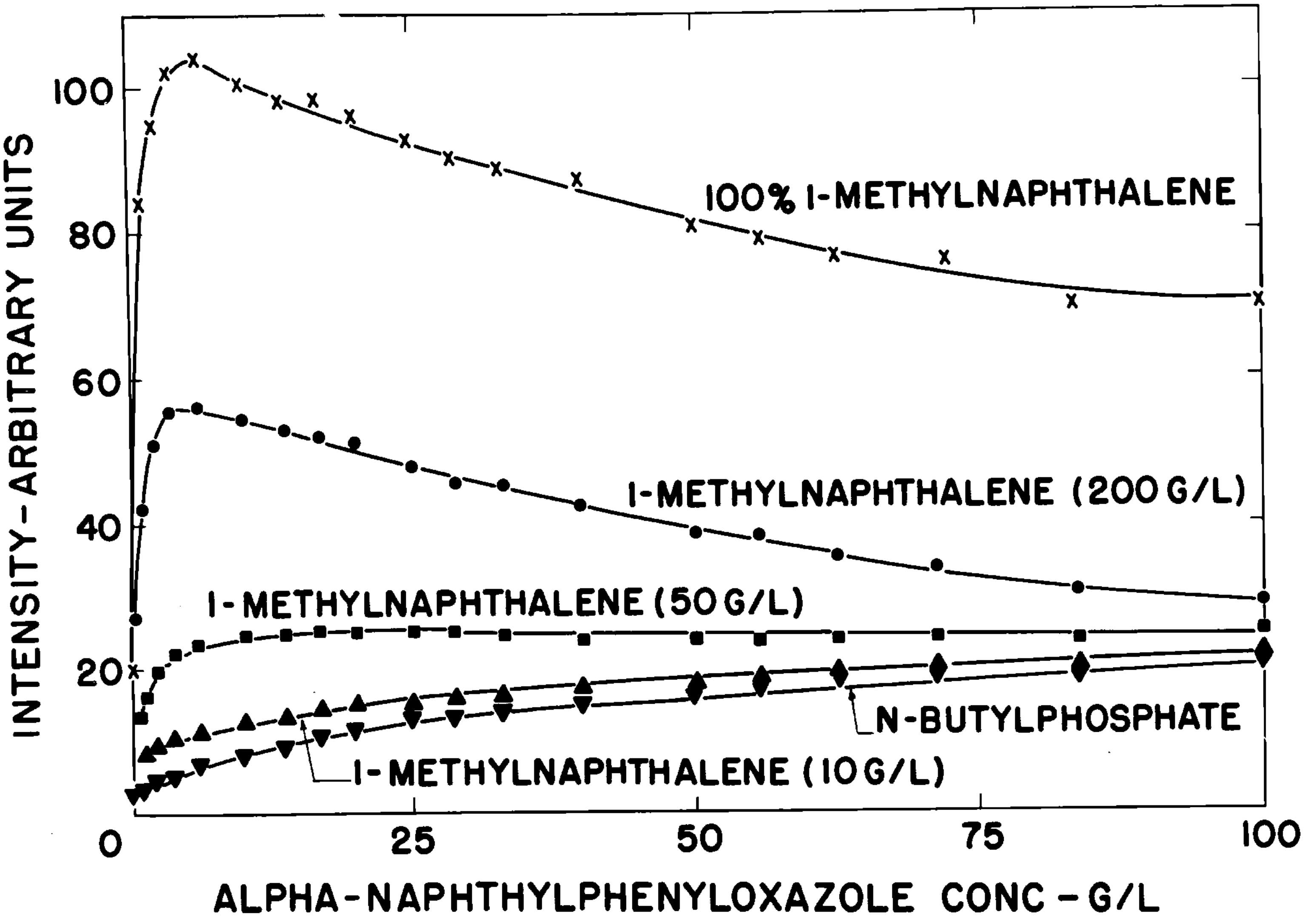

Fig. 7. Gamma ray induced fluorescence of α-naphthylphenyloxazole in combinations of n-butylphosphate and 1-methylnaphthalene.

decrease as $H^{\frac{n+1}{3}}$, until it reaches the value of the pure diffusion process 3. There are, however, other effects depending on H which influence the factors in Eq. 1. First, the viscosity of the system may change, and this would change δ for the material diffusion process; but this change is too small to account for the observed effects. τ_B and $\frac{N_A(\infty) - N_A(C_A)}{N_A(\infty)}$ also depend on H. The latter increases with decreasing H, as can be deduced from the curves of Fig. 7. If this increase is taken into account in Eq. 1, a change in $\frac{I_o}{I} - 1$ (quenching factor) is obtained which goes in a direction opposite to H, increasing with decreasing H if τ_B is assumed constant. It is difficult to state quantitatively the effect of changing H on τ_B, but there is little doubt that it increases with decreasing H. This would further increase the change of quenching with H.

In summarizing this investigation of the quenching of the bulk material as a function of its concentration in liquids, one comes to the following conclusions. Quenching decreases with decreasing concentration of bulk material. This accounts for the large difference in quenching of bulk molecules and of solute molecules. The discussion of Eq. 1 indicates further that the decrease of quenching is brought about by the simultaneous occurrence of processes 2 and 3 and by the decrease of the efficiency of process 2 with decreasing H. But the observed decrease in quenching is smaller than the decrease in δ because the term $\frac{N_A(\infty) - N_A(C_A)}{N_A(\infty)}$ increases with decreasing H. The estimated decrease in δ (under the assumption of constant τ_B) is almost proportional to H. This would indicate a considerable preponderance of the migration process over the material diffusion process, in solutions in undiluted bulk material. But final conclusions can be drawn only when the dependence of τ_B upon H has been investigated in detail.

From a practical viewpoint, these results indicate that when a quenching material must be in the solution, it is efficacious to increase the concentration of the solute and possibly dilute the bulk material.

A further remark is in order. In solutions in which an inactive diluent is used in the absence of added quencher, the efficiency of energy transfer decreases (larger Q) with decreasing H, which would also indicate that the migration part of process 2 decreases with increasing dilution. It may, however, be mentioned that Weinreb (9) did not find this change in Q in his investigations.

QUENCHING IN RIGID MEDIA

Previous investigation of energy transfer in rigid media has produced the following results. It is less effective than in liquids as seen from the general need of larger solute concentrations in order to extract the same amount of energy from plastics (e.g., polystyrene). Furthermore, the shape of the light emission versus concentration curves in polystyrene, for example, is quite different from that found in liquids. These results led to the conclusion that processes 1 and 2 are both effective in polystyrene since material diffusion (process 3) is excluded. The importance of process 2 in polystyrene was deduced from the strong quenching observed with various quenching agents. This quenching is too great at low quencher concentration to be accounted for by the random presence of an excited molecule near a quencher molecule. Solute quenching is smaller in plastics than in liquids. If naphthalene is added, energy transfer to the solute is enhanced as shown by the smaller solute concentration needed to extract equal energy in a plastic containing naphthalene but at the same time quenching is reduced for all quenching agents tested. An interpretation of this behavior is that transfer occurs mostly via process 1 and that the migration, involved in the quenching, is not so effective from naphthalene to naphthalene in the diluted system as from polystyrene to polystyrene. This is the same dilution effect discussed in the previous section for liquids.

In order to study the situation further, a plastic having the naphthalene group in its structure was investigated. In this manner, the concentration of naphthalene groups could be made much greater. It was hoped that discrimination then could be made between changes in migration efficiency brought about by the differences between naphthalene and benzene groups in the structure and those which are due to greater concentration. In a plastic containing naphthalene in its structure, energy migration would be expected to be better than in a system containing only dissolved naphthalene of concentration of a fraction of a mole per liter. Conditions otherwise would be expected to be similar, since in both cases naphthalene transfers the energy to the fluorescent solute.

Polyvinylnaphthalene was tested with various fluorescent solutes in the absence of added quenchers. It was found that these systems were as efficient as the best liquids with respect to the amount of light emitted and the solute concentration needed to extract the energy from the bulk. The initial part of the curves of light versus concentration was very similar to that observed in effective liquids (6). When α,α,α,α',α',α'-hexachloro-p-xylene was added, it was found that quenching is quite small even at higher quencher concentration (see Fig. 8). Since in liquids (inactive media containing large amounts of naphthalene or methylnaphthalene) naphthalene is strongly quenched by this agent, and since this compound also strongly quenches polystyrene without naphthalene, the conclusion would be that, contrary to expectation, migration does not occur to any large extent in polyvinylnaphthalene. This result was so surprising that polyvinylnaphthalene scintillators were also tested with diphenylmercury, which had been found to be very effective in quenching polystyrene and polystyrene plus naphthalene (10). Results are presented in Fig. 9. It is seen that quenching is strong even at small quencher concentrations; the molar half value concentration for quenching is close to that for energy transfer. This strong quenching at such low concentrations indicates the occurrence of process 2. These experiments offer strong evidence for the importance of the migration process in rigid media. Process 1 cannot be excluded for the energy transfer, but it is very likely excluded for the quenching reaction because diphenylmercury has no resonance with polyvinylnaphthalene. Since the half value concentration for quenching and fluorescence is relatively close, one may surmise that the migration process is of importance for energy transfer as well.

In order to understand the results with hexachloro-p-xylene, one possibility to be considered may be that quenching in some cases requires not only migration of excitation energy into the neighborhood of a quenching molecule but also the occurrence of a particularly close contact or specific orientation between the quencher and the excited molecule. In a liquid, this can result from reorientation or from the interaction of the two molecules. This may be more difficult in a plastic because of its rigidity. In the particular case of hexachloro-p-xylene, one might assume that the usual proximity of the excited molecule to the quencher is not enough to bring about quenching in polyvinylnaphthalene but is in polystyrene. This additional condition is apparently unnecessary for diphenylmercury, since in both polystyrene and polyvinylnaphthalene, diphenylmercury produces strong quenching.

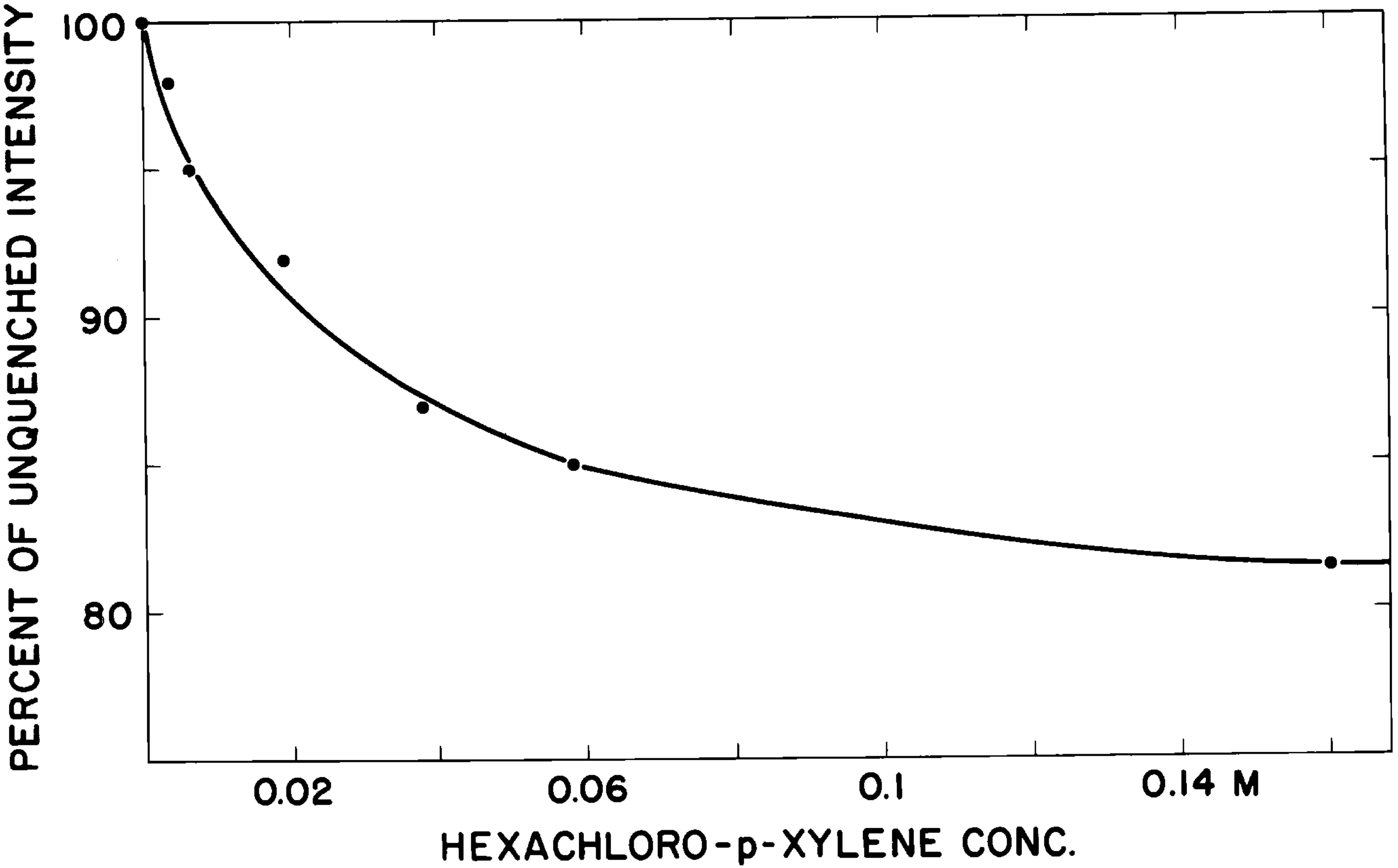

Fig. 8. Quenching of the gamma ray induced fluorescence of PVN/PPO (0.045 M) by α,α,α,α',α',α'-hexachloro-*p*-xylene.

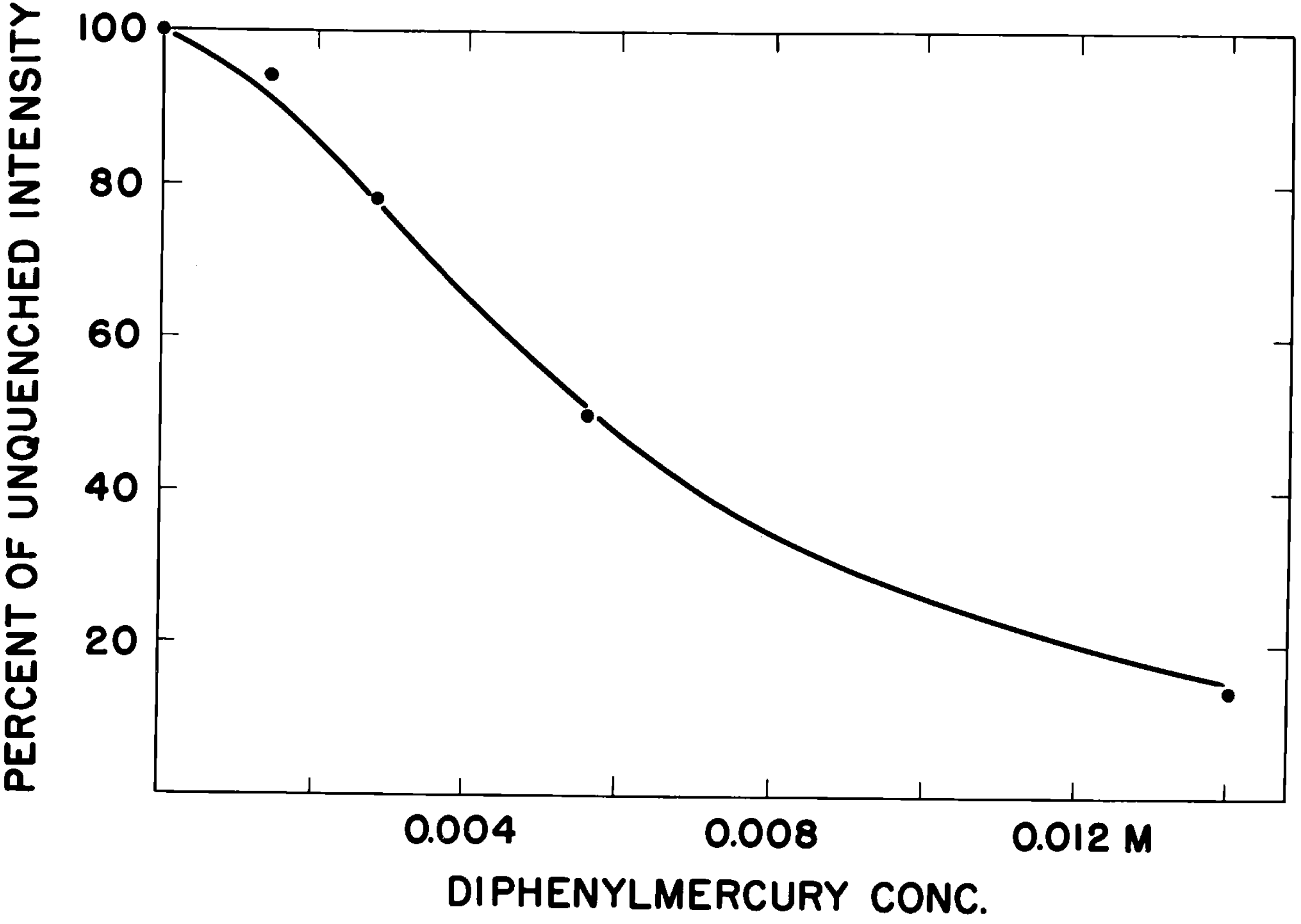

Fig. 9. Quenching of the gamma ray induced fluorescence of PVN/PPO (0.045 M) by diphenylmercury.

The results with plastics can be summarized as follows. Energy migration occurs in polyvinylnaphthalene and in polystyrene. In the former material, it is as good as in liquids assuming that in liquids the diffusion process is less effective than the migration process (Section 3). The closeness of the half value concentrations for quenching and for transfer indicates that process 1 is less important than the migration process. It is found that the mere propinquity of the respective molecules may not always be enough to bring about quenching.

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