

Fluorescence of Solutions Bombarded with High Energy Radiation (Energy Transport in Liquids)

Part II*

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In organic solutions containing fluorescent molecules a considerable part of the high energy radiation absorbed in the bulk material is transformed into light emitted by the fluorescent molecules. There is a transfer of excitation energy from the bulk material to these molecules which reaches its maximum at concentrations of approximately 1 g/l and higher. Experiments with mixed solvents are described where relatively small concentrations (several mole percent) especially of naphthalene and *o*-diphenylbenzene act in some way as a second solvent. The excitation energy can be localized by investigating the fluorescence of these mixed solvents when different fluorescent solutes are added. It is found that the energy migrates from the original solvent to the second solvent and then to the fluorescent molecule. This intermediate energy transfer can change the light emission curve completely. From this change the dependence of the light emission on internal and self-quenching could be determined. Besides this internal energy transfer, an energy transfer via radiation occurs which is described in detail by studying the absorption of the fluorescent light inside the solution by adding small amounts of a second solute of the order of 0.1 g/l. Such small amounts change the light intensity considerably and shift the spectrum to the spectrum of the second solute. Photographs and data of the spectral distribution of such solutions are presented, which show that such drifts already occur with very small amounts of the second solute.

A. INTRODUCTION

IN a previous paper, experiments on the light emission of dilute organic solutions excited by high energy radiation were described, and a theory was developed to explain the phenomena observed.¹ It was found that small amounts of solute molecules (of the order of 1 g/l) are already enough to increase the light emission of the pure solvent by as much as a factor of 35 and probably more. This phenomenon was explained by assuming a transfer of energy from the excited solvent molecules to the solute molecules. It was shown that the direct excitation of the same amount of solute as was present in the solution produced much smaller light emission than was observed in these experiments and therefore, could not be responsible for the large amount of light emitted. The energy transfer to the solute molecule was described as a competition between two processes: (1) the migration of the excitation energy through the solvent and its trapping by the solute molecule, and (2) the process of quenching the excitation energy in the solvent. These processes are described by means of a quenching probability $1/\tau_q$ which is inherent to the solvent, and a trapping probability $1/\tau_t$ which is a function of the concentration of the solute. In first approximation, $1/\tau_t$ was put equal to αc , where c is the concentration of the solute and α is a coefficient depending on both the solute and the solvent. The number, n , of excited solute molecules per second was given by

$$n = \alpha \tau_q c n_E (1 + \alpha \tau_q c)^{-1}, \quad (1)$$

where n_E represents the number of solvent molecules

directly excited per unit time. The intensity of the light emitted is then given by n times a factor which stems from the competition of three processes: the process of light emission by the solute molecule described by the probability $1/\tau_e$, the process of internal quenching (transformation of excitation energy into heat inside the solute molecule) described by the probability $1/\tau_i$ ($1/\tau_q$ has essentially the same physical significance of internal quenching as $1/\tau_i$ except that $1/\tau_q$ refers to the solvent molecule whereas $1/\tau_i$ refers to the solute), and the process of so-called self-quenching (interaction of solute molecules of the same kind) described by the probability $1/\tau_s$, which is as a first approximation also proportional to the concentration; i.e., equal to βc , where β depends on both the solute and the solvent. The radiation from the solvent is neglected in this development. The internal quenching probability is inherent to the solute molecule, but in some degree it depends on the surroundings of the molecule and, therefore, depends also on the solvent. In special cases it may even depend on the concentration of the solute. The final formula for light emission is given by (2), which is essentially the same expression as (2) of the previous paper:

$$I = \alpha \tau_q c n_E (1 + \alpha \tau_q c)^{-1} [1 + (\tau_e/\tau_i) + \beta \tau_e c]^{-1}. \quad (2)$$

The general shape of the light emission curve as a function of the concentration in most cases can be explained by this theory. It was found, however, that in several cases an additional phenomenon occurs; it was observed that very small concentrations of an additional solute (of the order of 0.5 g/l and less) could decrease the light emission considerably. This attenuation was attributed to an absorption of the light emitted from the first solute by the second solute and only

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¹ H. Kallmann and M. Furst, Phys. Rev. 79, 857 (1950).

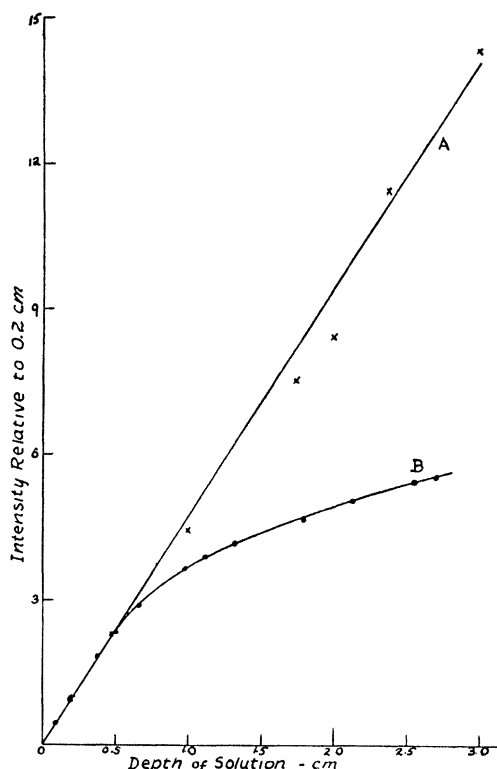


FIG. 1. Standard absorption curves.

partial retransformation of the energy into light. The rest of this energy is transformed into heat by the internal quenching in the second solute molecule.

Sections B and C are concerned with experiments bearing out the theory proposed in that paper. In Sec. B particularly the absorption of the fluorescent light in the solution is determined directly, whereas in Sec. C the emission spectra of a number of crystals and solutions is found. These latter spectra and their shift by small amounts of "impurities," play an important role in the theory. Solutions with strong absorption always show shifts of the spectrum of the emitted light of the original solution to that of the spectrum of the absorbing solute.

Section D describes experiments with mixed solutions where practically no absorption energy occurs, but where the maximum intensity of the emitted light and the concentration for maximum intensity are changed by the addition of fairly small amounts of an additional solute. Here one must assume a new process of energy transfer which, however, fits very well into the general scheme proposed in this paper. By means of these experiments one is able to follow the transfer processes in greater detail.

The experiments on absorption indicate that in some cases an energy transfer from the first solute to the second solute via radiation occurs. The question of whether such energy transfer by radiation may also be responsible for the energy transfer from the solvent to

the solute then arises. Since the radiation of the pure solvent is small compared with that of the solution, the energy transfer could be achieved only by means of radiation if the radiation emitted by this pure solvent is already strongly absorbed by the solvent itself within thicknesses considerably smaller than one millimeter. Otherwise, the small radiation of larger amounts of the pure solvent and the strong radiation of the same amount of solution could not be explained. Although the absorption experiments described in Sec. B do not indicate such a strong absorption, it may be that such an absorption could be overlooked, since a very thin layer of the pure solvent emits only a very small amount of radiation. Experiments described in Sec. D clearly prove that the energy transfer from the solvent to the solute does not occur by radiation. They indicate that another mechanism of energy transfer, for instance, such as that described in our previous paper, exists.

B. ABSORPTION EXPERIMENTS

In the previous paper (Table V) experiments were described showing that the intensity of a xylene-terphenyl solution was greatly attenuated by the addition of 0.1 g/l of anthracene. If this attenuation is caused by an absorption of the terphenyl radiation inside the solution, the ratio of the light intensities emitted by a pure xylene-terphenyl solution to that emitted by the contaminated solution should depend on the thickness of the solution under investigation. In a solution with small thickness the light has a smaller chance of being absorbed; and, therefore, the ratio of the light intensities of two solutions, one without and one with the absorber, should depend on the thickness and should approach unity for very small thicknesses of solutions. In the experimental arrangement described in the previous paper the intensity of the solution is not a linear function of the thickness of the solution, since the geometrical factor for different parts of the solution with respect to the source of radiation is not constant and the container has reflecting walls. To determine the effect of these factors, the intensity of the solution was measured as a function of the thickness of the solution with a 100-millicurie source relatively far away from the solution in a nonreflecting beaker. For this experiment the geometrical factor for all thicknesses of solutions was approximately the same, and if no absorption exists, the curve should be a straight line. Curve A in Fig. 1 clearly indicates that for a xylene-terphenyl solution practically no absorption exists. For checking other solutions, it was desirable to avoid using the strong 100-mc source. Therefore, the same xylene-terphenyl solution was measured as a function of the thickness in the old arrangement (but with an oxidized nonreflecting brass beaker instead of the porcelain beaker²) with the variable geometric factor. These measurements are

² A nonreflecting beaker was used, since it was found that by shifting the wavelength of the emitted radiation a difference in the reflection factor occurred.

represented by Curve *B* of Fig. 1. The ratio of these two curves gives the average geometrical factor for each depth of solution. To determine the absorption of other solutions, measurements were made with the old arrangement using the brass beaker, and the results compared with those of curve *B*. This xylene+terphenyl solution curve served as a standard for all other solutions. A typical experiment is described in Fig. 2, where *A* is the standard curve and curve *B* describes the light intensity curve as a function of the thickness in a xylene-terphenyl 1 g/l solution with an additional amount of 0.1 gram of anthracene per liter. Curve *B* is close to curve *A* for small thicknesses. The strong deviation for larger depths shows that anthracene absorbs the terphenyl radiation. As a further check that these deviations are due to absorption, an experiment was performed using two beakers, one above the other, the top one having a transparent bottom. The lower beaker contained a highly fluorescent terphenyl solution. The upper beaker was filled first with pure xylene; this xylene produced only a very slight attenuation. Then 0.1 g/l anthracene was dissolved in the solvent in the upper beaker, and the intensity of the terphenyl solution went down to 0.2 of its original value.

These absorption methods have been used to check whether solvents or solutions have their light emission attenuated by absorption through impurities and thus whether the fluorescence can be improved by further purification.³ A typical example is *o*-xylene of the highest purity obtainable commercially. With terphenyl this solvent exhibited a 20 percent smaller intensity than did the commercial ordinary xylene; our absorption check indicated noticeable absorption, larger than terphenyl in xylene. A comparison with a solution using *o*-xylene from a standard sample of the Bureau of Standards showed the same light emission with terphenyl as with ordinary xylene and the absorption check indicated much smaller absorption. This experiment shows that the commercially available *o*-xylene gives smaller readings than the normal xylene as a consequence only of absorption by impurities present. Some of our results are collected in Table I. They indicate that most of the solvents have some absorption in the ultraviolet in the region around 3000Å, but little absorption for wavelengths above 3400Å as was checked by the absorption curves of these solvents with terphenyl. All our solvents are checked with terphenyl (if it is soluble enough); and if they indicate no absorption with terphenyl radiation, these solvents are considered to be purified enough (for radiation around and above 3500Å). Additional purification would give no increase in light emission of the solute. The absorption observed in the ultraviolet seems to stem partly from unknown impurities. This was indicated by the following observation. If the light above about 3300Å was observed separately from the light emitted in the spectral range

below 3300Å (by means of a glass filter), it was always observed that the light more to the ultraviolet was attenuated by absorption, but that the light more to the visible showed little attenuation and in several cases even exhibited an increase in intensity above the values of the standard absorption curve. This seems to indicate that some light was transformed from the ultraviolet to the visible region.

The amount of absorption in the ultraviolet range is, however, not strong enough to explain the energy transfer from the solvent to the solute by radiation as can be seen, for example, from the values in Table I for benzene, which has an absorption curve in the ultraviolet fairly close to the standard curve. If the light emitted by the pure solvent were strongly enough absorbed to explain a radiation energy transfer in the solvent, a practically constant light intensity or even a decrease should be expected for thicknesses greater than about one millimeter.

Table I indicates that the absorption increases toward the ultraviolet. Benzene and phenylcyclohexane are the solvents which indicate the smallest absorption in the ultraviolet. This may be the reason why durene, with large ultraviolet fluorescence, gives the largest light emission in these solvents. How far the absorption in the "so-called" pure solvent comes from the solvent molecule itself is still an open question. With increasing wavelength the absorption decreases, as is evidenced by the fact that for the terphenyl radiation several solvents already show practically no absorption. Mesitylene,

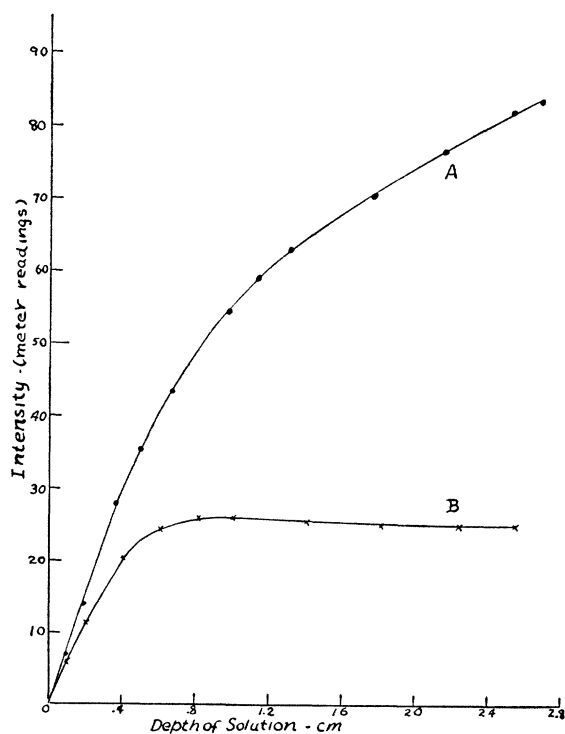


FIG. 2. Absorption in xylene+terphenyl (1 g/l)+anthracene (0.1 g/l).

³ H. Kallmann and M. Furst, *Nucleonics* 7, 69 (1950).

TABLE I. Absorption.

Solution	Depth cm	Approximate relative intensity to 0.2 cm		Solution	Depth cm	Approximate relative intensity to 0.2 cm	
		Solu- tion	Stand- ard			Solu- tion	Stand- ard
Benzene	2.5	4.8	5.4	Phenylcyclohexane+durene (10 g/l)			
Benzene ($\lambda < 3300$)	2.5	3.9	5.4	+ <i>o</i> -diphenylbenzene (0.5 g/l) ($\lambda > 3300$)	2.5	7.3	5.4
Benzene ($\lambda > 3300$)	2.5	6.7	5.4				
Benzene+durene (20 g/l)	2.6	4.4	5.5	Phenetole+phenyl alpha-naphthylamine (5.5 g/l)	2.5	4.9	5.4
Benzene+durene (20 g/l) ($\lambda < 3300$)	2.6	3.8	5.5				
Benzene+durene (20 g/l) ($\lambda > 3300$)	2.6	7.2	5.5	Xylene	2.5	3.2	5.4
				Xylene ($\lambda < 3300$)	2.5	2.6	5.4
Benzene+phenol (5 g/l)	2.6	2.9	5.5	Xylene ($\lambda > 3300$)	2.5	4.1	5.4
Benzene+phenol (5 g/l) ($\lambda < 3300$)	2.6	2.3	5.5				
Benzene+phenol (5 g/l) ($\lambda > 3300$)	2.6	3.3	5.5	Xylene+phenyl alpha-naphthylamine (7.5 g/l)	2.6	4.3	5.5
<i>p</i> -dioxane	1.9	3.2	4.9				
<i>p</i> -dioxane ($\lambda < 3300$)	1.9	1.6	4.9	<i>o</i> -xylene ^a	1.4	3.1	4.3
<i>p</i> -dioxane ($\lambda > 3300$)	1.9	5.6	4.9	<i>o</i> -xylene ^a ($\lambda < 3300$)	1.4	3.1	4.3
				<i>o</i> -xylene ^a ($\lambda > 3300$)	1.4	3.1	4.3
<i>p</i> -dioxane+terphenyl (5 g/l)	1.9	4.0	4.9				
iso-durene ^a	1.3	2.2	4.1	<i>o</i> -xylene ^a +terphenyl (6.5 g/l)	1.2	3.5	4.0
iso-durene ^a ($\lambda < 3300$)	1.3	2.1	4.1				
iso-durene ^a ($\lambda > 3300$)	1.3	3.0	4.1	<i>o</i> -xylene (commercial+terphenyl (7 g/l)	1.2	2.9	4.0
iso-durene+terphenyl (4 g/l)	1.1	3.4	3.9				
Mesitylene	2.6	1.8	5.5	<i>o</i> -xylene (commercial)	2.5	2.9	5.4
Mesitylene ($\lambda < 3300$)	2.6	1.0	5.5	<i>o</i> -xylene (commercial) ($\lambda < 3300$)	2.5	1.0	5.4
Mesitylene ($\lambda > 3300$)	2.6	2.4	5.5	<i>o</i> -xylene (commercial) ($\lambda > 3300$)	2.5	4.5	5.4
Mesitylene+terphenyl (5 g/l)	2.6	1.4	5.5				
Paraffin oil H-(CH ₂) _n -H	2.5	2.9	5.4	Xylene+anthranilic acid	2.6	5.2	5.5
Paraffin oil ($\lambda < 3300$)	2.5	1.3	5.4				
Paraffin oil ($\lambda > 3300$)	2.5	6.0	5.4	Xylene+terphenyl (1 g/l) ^b	2.6	5.5	5.5
				Xylene+terphenyl (1 g/l)+naphthalene (280 g/l)	2.6	4.4	5.5
Phenylcyclohexane C ₆ H ₅ C ₆ H ₁₁	2.5	3.6	5.4				
Phenylcyclohexane ($\lambda < 3300$)	2.5	3.3	5.4	Xylene+anthracene (2 g/l)	2.6	5.3	5.5
Phenylcyclohexane ($\lambda > 3300$)	2.5	5.7	5.4				
Phenylcyclohexane+durene (7.5 g/l)	2.5	3.5	5.4	Xylene+alpha-naphthylamine (2 g/l)	2.6	5.2	5.5
Phenylcyclohexane+durene (7.5 g/l) ($\lambda < 3300$)	2.5	3.1	5.4	Xylene+alpha-naphthylamine (2 g/l) +anthracene (0.08 g/l)	2.6	4.4	5.5
Phenylcyclohexane+durene (7.5 g/l) ($\lambda > 3300$)	2.5	5.4	5.4				
Phenylcyclohexane+terphenyl (4 g/l)	2.3	5.0	5.2	Xylene+fluoranthene (35 g/l)	1.9	4.4	4.9
				Xylene+fluoranthene (35 g/l)+ <i>o</i> -di- phenylbenzene (20 g/l)	1.9	4.3	4.9
Phenylcyclohexane+alpha-naphthyla- mine (1 g/l)	2.5	5.3	5.4				
				Xylene+terphenyl (1 g/l)+anthracene (0.1 g/l)	2.6	2.3	5.5
Phenylcyclohexane+phenyl alpha-naph- thylamine	2.4	4.7	5.3	Xylene+terphenyl (1 g/l)+naphthacene (0.05 g/l)	2.5	4.1	5.4
Phenylcyclohexane+durene (10 g/l)							
+ <i>o</i> -diphenylbenzene (0.5 g/l)	2.5	2.4	5.4	Phenylcyclohexane+durene (10 g/l)	2.0	2.8	5.0
Phenylcyclohexane+durene (10 g/l)				+naphthalene (0.5 g/l) ($\lambda < 3300$)	2.0	1.6	5.0
+ <i>o</i> -diphenylbenzene (0.5 g/l) ($\lambda < 3300$)	2.5	1.8	5.4	Phenylcyclohexane+durene (10 g/l)	2.0	4.9	5.0
				+naphthalene (0.5 g/l) ($\lambda > 3300$)	2.0	4.9	5.0

^a Bureau of Standards.^b Standard—see figures.

which has a large absorption (possibly owing to impurities) as a solvent, also shows a large absorption for terphenyl radiation. With alpha-naphthylamine and phenyl alpha-naphthylamine, anthranilic acid and fluoranthene radiation little if any absorption is observed. As already pointed out, strong absorption occurs with very small additions of anthracene and naphthacene because of their internal quenching. It was found that many substances, especially those emitting light of

longer wavelengths, have a variation with depth in different solvents similar to that of the standard curve. This can be considered as an independent check on the reliability of the absorption measurements. Only small absorption of the terphenyl radiation by as much as 280 g/l of naphthalene is found, although in this case the intensity went down by a factor of about 10. Also, the addition of *o*-diphenylbenzene to a fluoranthene solution produces practically no additional absorption,

though it does decrease the light emission noticeably (see Sec. D).

Table II describes how known "impurities" influence the intensity of these solutions. They show that many solutions are influenced by the addition of small amounts of other solutes. Absorption was always found if the attenuation already occurs with a very small concentration of the second solute (smaller than 0.5 g/l) as, for example, the cases of xylene solutions of alpha-naphthylamine or terphenyl by the addition of small amounts of anthracene. Some substances produce no attenuation at all, for instance, the addition of terphenyl to a xylene plus alpha-naphthylamine solution. With others, strong attenuating effects occur only with comparatively large concentrations of the second solute as in the addition of large amounts of naphthalene or *o*-diphenylbenzene to some of these solutions. Most of the attenuation in these latter cases does not stem from absorption but from other effects which will be described in Sec. D. With some substances, like diphenyl hexatriene, an addition of naphthalene or *m*-diphenylbenzene even, an increase in light output occurs (see also Table V of reference 1). A tentative explanation will be given in Sec. D.⁴

C. SPECTRAL DISTRIBUTION OF DIFFERENT SOLUTIONS AND POWDERS

To clarify the processes occurring in these solutions, measurements of the spectral distributions of the emitted light were carried out. Two different experimental arrangements were used; the first arrangement with which most of the spectra presented here were obtained consists of a highly reflecting silver tube of 10-cm length and about 2-cm diameter with a transparent quartz plate at one end which was placed directly in front of the slit of a quartz spectrograph. The solution was excited by a 100-millicurie gamma-source placed directly under the tube containing the solution. The photographic plate in the spectrograph was screened from the direct radiation of the source by some lead plates in order to reduce fogging. With this arrangement spectra of the emitted light of nearly all of the better solutions could be obtained by exposure for 16 hours; some weaker solutions required an exposure of 64 hours. This arrangement with a long tube is good for showing shifts in the emission spectra caused by absorption effects. Thus, if the solution contains even small amounts of impurities, the spectrum of the impurity could appear stronger than that of the original solution if the absorption theory is correct. The other experimental setup has been used to minimize absorption effects. In this case a very small amount of solution was used and the solution placed immediately above the slit of the spectroscope. The solution was energized by

TABLE II. Effects of known impurities.

Solution	Relative intensity
Xylene+alpha-naphthylamine (2 g/l)	0.19
Xylene+alpha-naphthylamine (2 g/l)+anthracene (0.04 g/l)	0.14
Xylene+alpha-naphthylamine (2 g/l)+anthracene (0.1 g/l)	0.13
Xylene+alpha-naphthylamine (2 g/l)+diphenyl (0.5-2 g/l)	0.19
Xylene+alpha-naphthylamine (1 g/l)+naphthalene (10 g/l)	0.075
Xylene+alpha-naphthylamine (1 g/l)+naphthalene (100 g/l)	0.019
Xylene+terphenyl (2 g/l)	0.39
Xylene+terphenyl (2 g/l)+anthracene (0.01 g/l)	0.21
Xylene+terphenyl (2 g/l)+anthracene (0.05 g/l)	0.15
Xylene+terphenyl (2 g/l)+fluoranthene (0.03 g/l)	0.16
Xylene+terphenyl (2 g/l)+ <i>o</i> -diphenylbenzene (0.5 g/l)	0.33
Xylene+terphenyl (2 g/l)+ <i>o</i> -diphenylbenzene (20 g/l)	0.09
Xylene+terphenyl (2 g/l)+naphthalene (0.3 g/l)	0.37
Xylene+terphenyl (2 g/l)+naphthalene (100 g/l)	0.060
Xylene+terphenyl (2 g/l)+anthranilic acid (0.1 g/l)	0.32
Xylene+phenyl alpha-naphthylamine (7.5 g/l)	0.24
Xylene+phenyl alpha-naphthylamine (7.5 g/l)+anthracene (0.1 g/l)	0.21
Xylene+phenyl alpha-naphthylamine (7.5 g/l)+anthracene (0.5 g/l)	0.16
Xylene+phenyl alpha-naphthylamine (2 g/l)	0.30
Xylene+phenyl alpha-naphthylamine (2 g/l)+fluoranthene (0.05 g/l)	0.24
Xylene+phenyl alpha-naphthylamine (2 g/l)+fluoranthene (0.2 g/l)	0.19
Xylene+anthranilic acid (3 g/l)	0.23
Xylene+anthranilic acid (3 g/l)+anthracene (0.5 g/l)	0.16
Xylene+anthranilic acid (3 g/l)+anthracene (3 g/l)	0.09
Xylene+fluoranthene (3 g/l)	0.12
Xylene+fluoranthene (3 g/l)+anthranilic acid (0.5 g/l)	0.12
Xylene+fluoranthene (3 g/l)+anthranilic acid (2 g/l)	0.12
Xylene+fluoranthene (3 g/l)+anthracene (0.5 g/l)	0.12
Xylene+fluoranthene (3 g/l)+anthracene (2 g/l)	0.11
<i>p</i> -dioxane+alpha-naphthylamine (2 g/l)	0.11
<i>p</i> -dioxane+alpha-naphthylamine (2 g/l)+naphthalene (30 g/l)	0.10
<i>p</i> -dioxane+alpha-naphthylamine (2 g/l)+naphthalene (100 g/l)	0.078
<i>p</i> -dioxane+phenyl alpha-naphthylamine (10 g/l)	0.11
<i>p</i> -dioxane+phenyl alpha-naphthylamine (10 g/l)+anthranilic acid (0.5 g/l)	0.10
<i>p</i> -dioxane+phenyl alpha-naphthylamine (10 g/l)+anthranilic acid (5 g/l)	0.09
Xylene+diphenylhexatriene (0.9 g/l)	0.21
Xylene+diphenylhexatriene (0.9 g/l)+ <i>m</i> -diphenylbenzene (0.5 g/l)	0.215
Xylene+diphenylhexatriene (0.9 g/l)+ <i>m</i> -diphenylbenzene (10 g/l)	0.245
Xylene+diphenylhexatriene (1 g/l)	0.22
Xylene+diphenylhexatriene (1 g/l)+phenyl alpha-naphthylamine (0.5 g/l)	0.24
Xylene+diphenylhexatriene (1 g/l)+phenyl alpha-naphthylamine (3 g/l)	0.26
Xylene+diphenylhexatriene (1 g/l)+phenyl alpha-naphthylamine (7 g/l)	0.24

⁴ These tables include substances giving considerable fluorescence, which were not mentioned in previous papers. Since the submission of the last paper many new solutions have been investigated. A summary of these results may be published soon.

a polonium alpha-particle source of 10-millicurie strength. With this source, spectra could be obtained from the best solutions within five hours; fog was completely absent from these plates.

TABLE III. Spectral ranges of different solutions and crystals.

Substance	Approximate emission spectral range (Angstroms)
Anthracene crystal	4200-4700
Xylene+anthracene (1.5 g/l)	3900-4400
Naphthalene crystal	3300-3800
Xylene+naphthalene (20 g/l)	3200-3800
Durene crystal*	2900-3300
Phenylcyclohexane+durene (4 g/l)	2800-3500
Phenylcyclohexane+durene (4 g/l)+fluoranthene (0.1 g/l)	4000-5000
Phenylcyclohexane+durene (4 g/l)+fluoranthene (1 g/l)	4000-5000
Phenylcyclohexane (α -particles)	2700-3100
Xylene+fluoranthene (3 g/l)	4100-5000
Tetrahydronaphthalene+fluoranthene (3 g/l)	4200-5500
Phenylcyclohexane+terphenyl (3 g/l)	3200-4100
Phenylcyclohexane+terphenyl (1 g/l) (α -particles)	3150-4000
Xylene+terphenyl (1 g/l)	3250-4000
Xylene+terphenyl (1 g/l)+anthranilic acid (0.1 g/l)	3600-4400
Xylene+terphenyl (2 g/l)+anthracene (0.05 g/l)	3800-4400
<i>p</i> -cymene+terphenyl (2.5 g/l)	3300-4000
Phenylcyclohexane+terphenyl (3 g/l)+diphenylhexatriene (trace)	3200-4800
Tetrahydronaphthalene+terphenyl (5 g/l)	3500-4000
Terphenyl crystal	3600-4300
Xylene+ <i>m</i> -diphenylbenzene (15 g/l)	3200-4000
Xylene+ <i>m</i> -diphenylbenzene (15 g/l) (α -particles)	3200-3800
Xylene+anthranilic acid (3 g/l)	3600-4400
Xylene+diphenylhexatriene (0.6 g/l)	4000-5500
Phenylcyclohexane+diphenylhexatriene (1 g/l) (α -particles)	3900-5500
Xylene+ α -naphthylamine (2 g/l)	3600-4400
Xylene+ β -naphthylamine (2 g/l)	3700-4300
Xylene+ α -naphthylamine (2 g/l)+anthracene (0.1 g/l)	3800-4400
Phenylcyclohexane+phenyl α -naphthylamine (1 g/l)	3700-4500
Xylene+phenyl α -naphthylamine (2 g/l)	3200-4500
Xylene+phenyl α -naphthylamine (2 g/l)+fluoranthene (0.2 g/l)	3900-4500
<i>p</i> -dioxane+phenyl α -naphthylamine (5 g/l)	3900-4500
Aniline+phenyl α -naphthylamine (1.5 g/l) (α -particles)	3800-4500
Phenanthrene powder (α -particles)	3800-4400
Phenylcyclohexane+phenanthrene (7 g/l) (α -particles)	3800-4100
Phenylcyclohexane+carbazole (1 g/l) (α -particles)	3400-3800
Phenylcyclohexane+diphenylbutadiene (1 g/l) (α -particles)	3600-4200
Phenylcyclohexane+ <i>o</i> -diphenylbenzene (20 g/l) (α -particles)	3600-4500

* The durene crystal of one-cm cube was prepared for us by Mr. J. Zar.

The results are listed in Table III in which the range of the more intense part of the spectrum is indicated. For comparison purposes, the spectrum of the crystal was also determined for some substances. Terphenyl and anthracene spectra using x-rays and light have recently been published by Harrison and Reynolds.⁵ Our spectra of these substances obtained with gamma-rays agree closely with their spectra, thus indicating that they do not strongly depend on the kind of excitation (see also end of this section).

The comparison between the pure crystal and the solution indicates that the solution spectrum is in some cases broader than the spectrum of the pure crystal and

⁵ F. B. Harrison and G. T. Reynolds, Phys. Rev. 79, 732 (1950).

somewhat shifted to the ultraviolet. Special notice should be given to the results with naphthalene. The naphthalene crystal was a large clear crystal and gave a spectrum between 3300 and 3800A. The same crystal was tested on a multiplier tube and compared with an anthracene crystal. Its peak intensity was about 40 percent of that of anthracene. In this case we can conclude from the spectrum that the light emitted from this crystal was the light of the naphthalene and not from any impurity, since this spectrum of the crystal coincides so closely with the spectrum of a xylene+naphthalene solution that it could not be excited by energy transfer inside the crystal from the bulk material to an unknown impurity. Energy transfer to small amounts of additional material occur with larger probability only if the emission spectrum of the additional material is far enough toward longer wavelengths from the emission spectrum of the bulk material; otherwise, no trapping of the excitation energy can occur in the additional molecules. These ideas are supported by an experiment described in Sec. D.

These spectra further support the idea that the effects of small amounts of additional material stem from absorption. Table III indicates that the spectrum of 4 g/l of durene in a phenylcyclohexane solution ranges from 2800 to 3500A. With 0.1 g/l of fluoranthene added to this solution, the spectrum is already completely shifted to the fluoranthene spectrum (see Table III). With 0.05 g/l of anthracene added to a xylene-terphenyl solution of 2 g/l the spectrum was completely removed from the region of terphenyl to that of anthracene. With such a small amount of anthracene alone, no spectrum at all

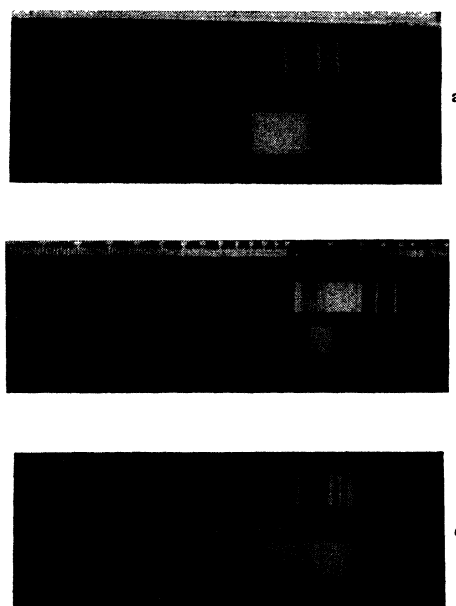


FIG. 3. (a) Terphenyl solution. (b) Terphenyl solution +0.1 g/l anthranilic acid. (c) Terphenyl solution+trace of diphenylhexatriene.

would be obtained for the same duration of exposure. A similar result was obtained by adding 0.1 g/l of anthranilic acid to a xylene-terphenyl solution; the spectrum is completely shifted to the region of the anthranilic acid. Figure 3 gives some typical spectra obtained; Fig. 3a presents the spectrum of a terphenyl solution, 3b the spectrum of a terphenyl solution with 0.1 g/l anthranilic acid added, it shows the complete shift to the anthranilic acid spectrum, 3c gives the spectrum of a terphenyl solution with a trace of diphenylhexatriene. Here both spectra, that of terphenyl and that of diphenylhexatriene, appear in agreement with results obtained from absorption measurements.

A special search has been made with this method for substances excited by gamma-radiation which gives an emission more to the visible. The best substance found is diphenylhexatriene, which gives a high intensity and a spectrum of which reaches to about 5500Å. Another substance with fairly good light efficiency in the same region is fluoranthene. This absorption phenomenon may be helpful in scintillation counter work. It gives the possibility of shifting the spectra of a given solution to the visible by using only very small amounts of a substance. This may be of advantage for the reason that the intensity of the emitted light in the visible can, in some cases, be made even larger than by using this substance directly, since the self-quenching effect can thus be avoided. In cases where the substance contains small amounts of quenching impurities, the effects of these impurities may be minimized by the absorption method. Finally, some of these substances are rather costly, and the absorption method is less expensive.

The spectra of the pure solvents would be too weak to be observed with the long tube arrangement because the fog produced by the gamma-radiation is too high. With the arrangement using alpha-particles for excitation such measurements can be made. Phenylcyclohexane has an emission spectrum between 2700 and 3100Å. It appears that the spectra excited by alpha-particle excitation coincide fairly closely with the spectra taken with the gamma-radiation arrangement, provided that no absorption occurs.

D. EXPERIMENTS WITH MIXED SOLUTIONS

As was indicated in Sec. B, quite different effects occur in mixed solutions. All of these effects seem to be complicated by the absorption of the light emitted from one substance by the other substances. To find out more about these processes in mixed solutions we have used two substances in which little if any absorption occurs. These substances are naphthalene and *o*-diphenylbenzene. The emission and absorption spectra of naphthalene are so similar to those of terphenyl that no absorption of the terphenyl radiation can occur. Since most of the substances under investigation have emissions of longer wavelengths than those of terphenyl, the light emitted by them cannot be absorbed by naphthalene. Only substances like durene have an emission

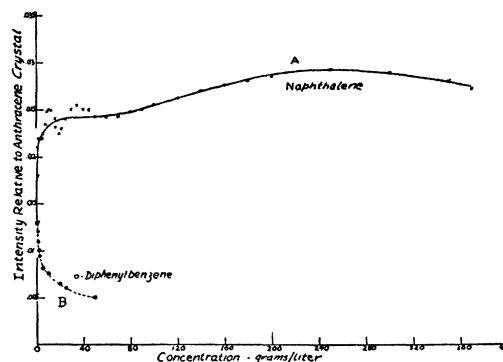


Fig. 4. Naphthalene and *o*-diphenylbenzene in xylene.

spectrum which could be absorbed by naphthalene. These conclusions are verified with solutions containing naphthalene; the durene emission is decreased by absorption, but not the light emitted by most of the other substances investigated. *O*-diphenylbenzene also has an absorption spectrum similar to that of *p*-diphenylbenzene (terphenyl) and, therefore, cannot absorb the emission of most of the substances used in these experiments.

Either of these substances added to the solvents under investigation were found to emit only a very small amount of light. For example, naphthalene in xylene has a maximum intensity of 1/15 of a corresponding terphenyl solution; *o*-diphenylbenzene perhaps emits no light at all; it even weakens the small light intensity emitted by the pure solvent. The light emission curves of naphthalene and of *o*-diphenylbenzene in xylene are given respectively by curves A and B of Fig. 4. The light curve of naphthalene gives the intensity of a solution for the same amount of xylene.† There is a sharp increase at small concentrations and a leveling off at about a concentration of 5 g/l. Since the density of the solution is practically unchanged by the addition of naphthalene, and since the parts of the solution remote from the source in this case contribute but little to the total intensity, this increase in emitted radiation is only very slightly due to the larger amount of substance used in the naphthalene experiments. This curve coincides in its general shape with the curves published by Ageno, Chiozzotto, and Querzoli.⁶ It may be noted that the values near the leveling-off concentration show a noticeable fluctuation. The *o*-diphenylbenzene curve shows a decrease in intensity with concentration. Measurements taken with a previous sample of *o*-diphenylbenzene obtained from the same company showed, however, another type of variation. There was a small gradual increase in intensity over a large range of concentration but no sharp rise at small concentration

† Note added in proof.—It may be that the small light output of the naphthalene solution is due to oxygen in the solution, since a characteristic quenching by oxygen of naphthalene radiation is reported in the literature. However, the measurements below indicate that the energy is not quenched.

⁶ Ageno, Chiozzotto, and Querzoli, *Phys. Rev.* **79**, 720 (1950).

TABLE IV. Effects of naphthalene and *o*-diphenylbenzene.

Solution	Relative intensity
Xylene+alpha-naphthylamine (1 g/l)	0.18
Xylene+alpha-naphthylamine (1 g/l)+naphthalene (10 g/l)	0.075
Xylene+alpha-naphthylamine (1 g/l)+naphthalene (100 g/l)	0.019
<i>p</i> -dioxane+alpha-naphthylamine (2 g/l)	0.11
<i>p</i> -dioxane+alpha-naphthylamine (2 g/l)+naphthalene (100 g/l)	0.08
Toluene+alpha-naphthylamine (1 g/l)	0.18
Toluene+alpha-naphthylamine (1 g/l)+naphthalene (100 g/l)	0.04
Xylene+anthracene (1.5 g/l) ^a	0.07
Xylene+anthracene (1.5 g/l) ^a	0.07
Xylene+anthracene (4 g/l)+ <i>o</i> -diphenylbenzene (50 g/l) ^a	0.023
Xylene+anthracene (1.5 g/l)+naphthalene (230 g/l) ^a	0.07
Xylene+phenyl alpha-naphthylamine (2 g/l) ^a	0.31
Xylene+phenyl alpha-naphthylamine (9 g/l)+ <i>o</i> -diphenylbenzene (50 g/l) ^a	0.11
Xylene+anthranilic acid (2 g/l) ^a	0.24
Xylene+anthranilic acid (2 g/l)+naphthalene (20 g/l) ^a	0.24
Xylene+anthranilic acid (4 g/l)+ <i>o</i> -diphenylbenzene	0.075
<i>p</i> -cymene+anthranilic acid (4 g/l) ^a	0.17
<i>p</i> -cymene+anthranilic acid (3 g/l)+naphthalene (20 g/l) ^a	0.20
Xylene+fluoranthene (3-8 g/l) ^a	0.13
Xylene+fluoranthene (3-8 g/l)+naphthalene (20 g/l) ^a	0.13
Xylene+fluoranthene (18-35 g/l)+ <i>o</i> -diphenylbenzene (20 g/l) ^a	0.09
<i>p</i> -cymene+fluoranthene (7 g/l) ^a	0.11
<i>p</i> -cymene+fluoranthene (20 g/l)+ <i>o</i> -diphenylbenzene (20 g/l) ^a	0.082
Phenylcyclohexane+terphenyl (2.5 g/l)	0.38
Phenylcyclohexane+terphenyl (2.5 g/l)+ <i>o</i> -diphenylbenzene (0.5 g/l)	0.29
Phenylcyclohexane+terphenyl (2.5 g/l)+ <i>o</i> -diphenylbenzene (5 g/l)	0.095
Xylene+ <i>m</i> -diphenylbenzene (0.5 g/l)	0.056
Xylene+ <i>m</i> -diphenylbenzene (0.5 g/l)+ <i>o</i> -diphenylbenzene (1 g/l)	0.044
Xylene+ <i>m</i> -diphenylbenzene (0.5 g/l)+ <i>o</i> -diphenylbenzene (10 g/l)	0.014
Phenylcyclohexane+durene (5 g/l)	0.057
Phenylcyclohexane+durene (5 g/l)+ <i>o</i> -diphenylbenzene (0.5 g/l)	0.015
Xylene+diphenylhexatriene (1.5 g/l) ^a	0.235
Xylene+diphenylhexatriene (1 g/l)+naphthalene (20 g/l) ^a	0.24
Xylene+diphenylhexatriene (2.5 g/l)+ <i>o</i> -diphenylbenzene (20 g/l) ^a	0.069
Xylene+diphenylhexatriene (1 g/l)+naphthalene (100 g/l)	0.28
Xylene+terphenyl (2 g/l)	0.39
Xylene+terphenyl (2 g/l)+naphthalene (0.3 g/l)	0.37
Xylene+terphenyl (2 g/l)+naphthalene (100 g/l)	0.08
Xylene+terphenyl (7 g/l) ^b +naphthalene (20 g/l) ^a	0.24
Xylene+terphenyl (2 g/l)+ <i>o</i> -diphenylbenzene (0.1 g/l)	0.37
Xylene+terphenyl (2 g/l)+ <i>o</i> -diphenylbenzene (20 g/l)	0.24
Xylene+terphenyl (7 g/l) ^b + <i>o</i> -diphenylbenzene (20 g/l) ^a	0.17

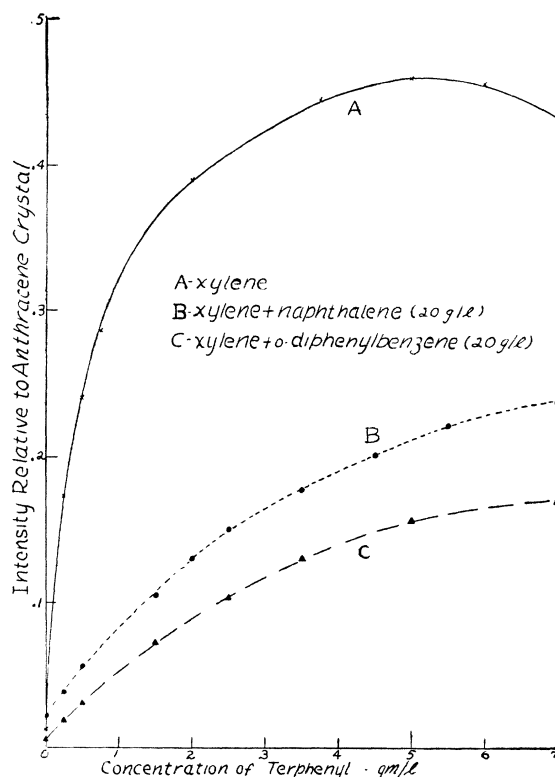
^a Approximate maximum intensity.^b Saturated.

FIG. 5. Terphenyl solutions.

of a fluorescent contamination in the more fluorescent sample of *o*-diphenylbenzene. This assumption was borne out by obtaining a spectrum of the more fluorescent solution with the aid of α -particles. It was found to extend to 4500Å. It may be mentioned that both types of *o*-diphenylbenzene solutions showed no difference of behavior with respect to the addition of different fluorescent material.

Similar curves are found when these substances are dissolved in other solvents. Since the emission spectra of these substances are close to that of terphenyl [for naphthalene this is proved by our experiments of Sec. C and for *o*-diphenylbenzene it can be derived from the experimental fact that the absorption spectra of *o*-diphenylbenzene and *p*-diphenylbenzene (terphenyl) nearly coincide], the possibility of energy transfer to these substances should be as good as for terphenyl itself. Since, however, the intensities are much lower, the idea presents itself that the energy still goes over to these molecules but is quenched before the light is emitted. According to Eq. (2) this would mean a very small value τ_i for these substances.

To test this idea and to find out what happens to the excitation energy in these solutions with naphthalene and *o*-diphenylbenzene, we have introduced into them molecules of other solutes normally highly fluorescent in pure solvents. The results are collected in Table IV and Figs. 5, 6, 7, and 8. These experiments show that for the fluorescent substances with emission spectra

as with the naphthalene curve. The difference between the two samples was due most likely to a small amount

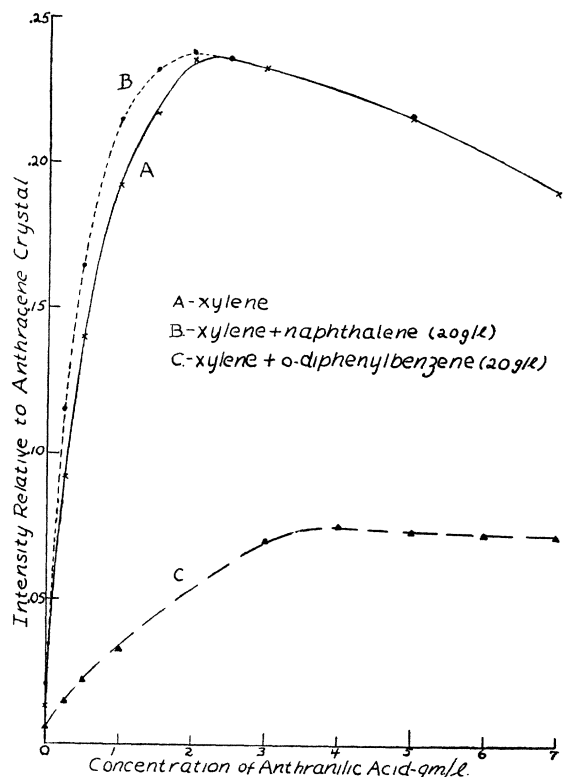


FIG. 6. Anthranilic acid solutions.

close to those of naphthalene or *o*-diphenylbenzene, the light intensity is much smaller in these solutions than in the pure solvent. With large naphthalene or *o*-diphenylbenzene concentrations the light emission, for example, of a terphenyl solution, is strongly suppressed for a given concentration of terphenyl. The intensity continues to go down with increasing naphthalene or *o*-diphenylbenzene concentration and approaches the light emission of these substances without terphenyl (see Table IV and Fig. 5). Phenyl alpha-naphthylamine is not as strongly attenuated as terphenyl. It must be emphasized that strong changes are already achieved with the relatively small concentration of one percent of these solutes. These effects are not caused by absorption as can be seen from absorption curves taken with these solutions. With substances such as fluoranthene, anthracene, anthranilic acid, and diphenyl hexatriene, having emission spectra more toward the visible than terphenyl, the results are completely different. In naphthalene solutions the light emission is only slightly affected; practically the same light emission curves as functions of the concentration are obtained if these substances are dissolved in xylene-naphthalene solutions instead of pure xylene. In some cases even a slight increase in light emission is observed (see Fig. 8 and Table IV).

With *o*-diphenylbenzene-xylene solutions, however, the light emission curves of these substances are greatly changed; all their maximum concentrations are shifted

to higher concentrations even by small amounts of *o*-diphenylbenzene. The maximum light intensities of anthranilic acid and of anthracene are more strongly reduced than that of fluoranthene (see Figs. 6 and 7 and Table IV). Similar results are obtained with different solvents such as cymene and dioxane; only the quantitative behavior is different. For dioxane with *o*-diphenylbenzene, for instance, phenyl alpha-naphthylamine gives a relatively higher light emission than in a xylene-*o*-diphenylbenzene solution as compared to the reading in the pure solvent; but again the maximum concentration is shifted to larger concentrations (see Table IV).

There are two possible explanations for these effects based on Eq. (2). The first assumes that the internal quenching constants τ_i of naphthalene and of *o*-diphenylbenzene are much smaller than those of terphenyl, anthranilic acid, and other fluorescent substances. This means that the excitation energy is mostly internally quenched before it can be emitted as light. The transfer of excitation energy from the solvent to these molecules may be of the same order of magnitude as for terphenyl or for other substances. With 20 grams or more per liter of naphthalene or *o*-diphenylbenzene a considerable amount of excitation energy is transferred from the solvent to these molecules. If now other molecules which are highly fluorescent are introduced in small concentrations, the energy passes first to the naphthalene or the *o*-diphenylbenzene molecules and then from these molecules to the fluorescent molecules. For this latter

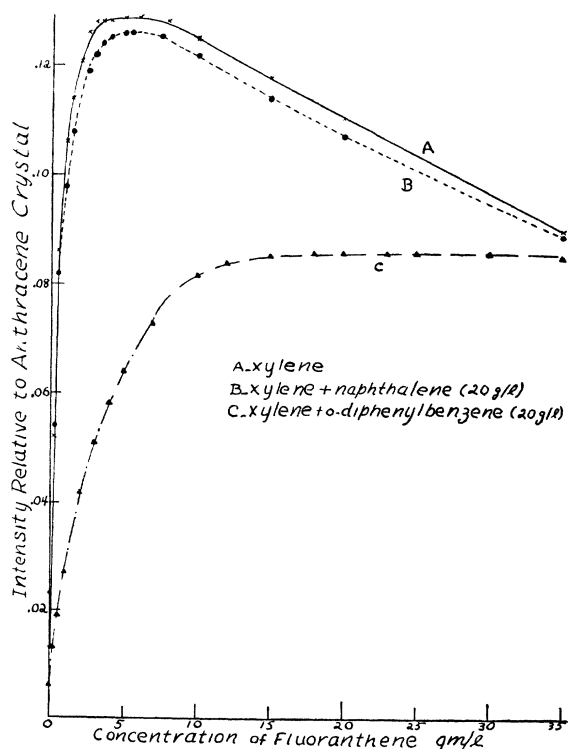


FIG. 7. Fluoranthene solutions.

energy transfer the coefficient α and the constant τ_q in Eq. (1) are those belonging to naphthalene or *o*-diphenylbenzene and not to xylene.⁷ If we now assume that $\alpha\tau_q$ is practically the same for naphthalene as for xylene, the behavior of anthranilic acid, anthracene, and fluoranthene in naphthalene solutions can be understood. For terphenyl, however, it cannot be assumed that α is still the same for the energy transfer from naphthalene to terphenyl as from xylene to terphenyl, since the emission spectra of terphenyl and naphthalene are too close to each other. There is then little trapping of the excitation energy by the terphenyl molecule, since the energy can also go back from the terphenyl to the naphthalene. Thus terphenyl can draw most of its energy only from the xylene. If the terphenyl concentration is high enough, the energy transfer from the xylene will be divided between naphthalene and terphenyl, and a certain amount of energy will still go directly to the terphenyl molecule and be emitted as light by this molecule. Therefore, the light emitted by such a solution should depend strongly on the concentration ratio of terphenyl and naphthalene or terphenyl and *o*-diphenylbenzene and should increase with an increase of this ratio until self-quenching becomes considerable. As a consequence, the maximum in such solutions is shifted toward higher concentrations of the fluorescent molecules. This occurs also with naphthalene, where other substances such as diphenyl hexatriene exhibit a shift to smaller concentration, since in this case $\alpha\tau_q$ is larger than for the original solvent. Other substances with absorption and emission spectra close to those of naphthalene and *o*-diphenylbenzene should behave in a similar manner. This is just what was observed.

For *o*-diphenylbenzene, τ_i must be assumed to be much smaller than for naphthalene, and therefore also smaller than for xylene, as was indicated by the fact that *o*-diphenylbenzene shows practically no light emission at all. If it is assumed in a similar manner that the energy goes at first to *o*-diphenylbenzene and from this molecule to the other molecules, then τ_q for the energy transfer from *o*-diphenylbenzene to other molecules is essentially given by the internal quenching τ_i of *o*-diphenylbenzene (see footnote 7). Since this latter τ_i is very small, the τ_q value for this combined solution must be even smaller than the value in the original solvent. That τ_i for *o*-diphenylbenzene is really very small can be seen from another experiment: if 0.1 g/l of *o*-diphenylbenzene is introduced into a solution of durene and xylene which emits a fairly strong ultraviolet radiation, the radiation is quenched. This means that the durene radiation is absorbed by *o*-diphenyl-

benzene and only a very small fraction re-emitted as light, which shows the high internal quenching probability of *o*-diphenylbenzene.

For all substances with an absorption and an emission spectrum close to that of *o*-diphenylbenzene, an energy transfer does not occur, for the reasons given above for naphthalene. Only for substances with spectra more to the visible than that of *o*-diphenylbenzene can an energy transfer be expected, but for these the τ_q value should be smaller than that in xylene. From (2) it follows that all maximum concentrations should in such cases be shifted to larger concentrations and also that the maximum intensity should decrease. These are just the results which were observed with anthranilic acid, anthracene, and fluoranthene in xylene-*o*-diphenylbenzene solution (see Figs. 6, 7, and Table IV). The slope of the curve describing the increase of intensity with increasing concentration of these solutions is much smaller than for the pure solvent solution; the maximum intensity in the case of fluoranthene is diminished only by 1.5 and for the other two substances it is decreased by a factor of about 3. This is just what can be expected from formula (2).

Physically these effects can be understood in the following way. The energy going to the fluoranthene molecule must be drawn from the *o*-diphenylbenzene molecule. Since the excitation energy possesses a shorter lifetime in this molecule (because of the large internal quenching) than in the xylene molecule, a higher concentration of fluoranthene is needed to draw the same amount of energy from *o*-diphenylbenzene than from xylene. With higher concentration of fluoranthene self-quenching is increased; but if the self-quenching effect is not too large, the maximum intensity will not be diminished too strongly. In anthranilic acid and also in anthracene the same effect occurs; but since the self-quenching of these substances is comparatively high, the maximum value of the light emission is smaller in *o*-diphenylbenzene than in xylene. The smaller self-quenching of fluoranthene can be deduced from the flatness of its light curve after the maximum concentration in xylene solutions is reached.

The other possibility of explaining the behavior of these mixed solutions would be to assume, in order to account for the small light emission of the solutions of naphthalene and *o*-diphenylbenzene in xylene and other solvents, that practically no energy transfer to the naphthalene molecule or the *o*-diphenylbenzene molecule occurs. However, we can find no good theoretical reason for such an abnormal behavior of these substances. Nevertheless, on this assumption one could perhaps partly account for the behavior of the mixed solutions with naphthalene. According to this idea, the additional fluorescent molecules in these solutions draw their energy entirely from the xylene. The fact that those molecules, having emission spectra near that of naphthalene, show a strong decrease in intensity could be explained by the further assumption that there is an

⁷ Note that τ_q has essentially the meaning of internal quenching within the solvent molecule which transfers its excitation energy directly to the fluorescent molecule. In the above cases, however, for high concentrations the naphthalene and *o*-diphenylbenzene molecules transfer the excitation energy to the fluorescent molecules; therefore, for τ_q the internal quenching constants of these molecules must be used.

interaction between these fluorescent molecules and the naphthalene molecules similar to that between like molecules, and that the naphthalene molecule quenches the radiation of molecules with a similar light emission spectrum by the mechanism of self-quenching. Thus, the light emission of such molecules is weakened with increasing naphthalene concentration. Substances with emission spectra strongly displaced towards the visible from the emission spectrum of naphthalene, however, are not influenced by naphthalene and some self-quenching mechanism, since their spectra are too different from each other. Therefore, these substances are only slightly influenced in their light emission even by large concentrations of naphthalene, since it is assumed in this explanation that they draw all their energy directly from xylene.

Such an assumption would not hold, however, for the *o*-diphenylbenzene solution since here already relatively small amounts of *o*-diphenylbenzene (1 mole percent solution) strongly influence the shape of the light curve in such a way as to reduce the light intensity for a given concentration of the fluorescent molecule. This effect can be much better understood if one assumes that the energy first goes to the *o*-diphenylbenzene and then from this molecule to the respective fluorescent molecule. We suppose, however, that the same mechanism is also valid for naphthalene. That this may be so can be seen from experiments with *p*-cymene as the initial solvent, and additional amounts of naphthalene. In such a solution the fluorescence of anthranilic acid is already increased by small amounts of naphthalene, and the light concentration curve is shifted to the left. This means that in this case the internal quenching probability of naphthalene $1/\tau_i$ is smaller than for the cymene molecule. Therefore, the energy transfer via the naphthalene molecule is more effective than the direct energy transfer from cymene to the anthranilic acid molecule. Another hint in this direction may be seen in the fact that diphenylhexatriene in xylene also shows the effect of increasing intensity with larger amounts of naphthalene (Fig. 8). The addition of *m*-diphenylbenzene has also been found to produce an even slightly greater increase in the intensity of diphenylhexatriene. Thus, the first mechanism of the energy transfer taking place via the additional solute molecule seems to provide the more adequate explanation.

The advantage of using just these mixed solutions for exploring the mechanism of energy transfer lies in the fact that small amounts of additional substances already strongly influence the shape of the light curve (see Figs. 5 to 8, and Table IV), and give comparatively no light emission of their own, so that they do not mask the main fluorescence. There are several parameters describing the light emission from the fluorescent molecule in solution (Sec. A); most of them depend on the properties of the solvent, but they should change only slightly if the solvent is also changed only slightly by a relatively small percentage of added naphthalene

or *o*-diphenylbenzene. If the idea of energy transfer to these substances from the initial solvent and its further transfer from these molecules to the fluorescent solutes is correct, then $\alpha\tau_q$ in (2) has to be chosen for the transfer from naphthalene or *o*-diphenylbenzene and not from the original solvent. Since the energy transfer to naphthalene and *o*-diphenylbenzene already occurs at small concentration, this factor $\alpha\tau_q$ goes over from the original value to the values inherent in these molecules even when only small amounts of such molecules are added. The other constants indicated are not changed by small amounts of additional substances and especially the self-quenching coefficient β may be influenced only very slightly as long as the emission spectra of the different molecules are not close to each other.

There is another point which is explained by these experiments, namely, that the possibility of energy transfer from the solvent to the molecule by radiation is ruled out. If there should be some hidden radiation which is already strongly absorbed within small thicknesses of solution, then this radiation would go over to the naphthalene or *o*-diphenylbenzene molecule by absorption since radiation strongly absorbed in xylene is still more strongly absorbed by *o*-diphenylbenzene. *O*-diphenylbenzene, however, quenches any absorbed radiation, as is proved by the experiments of adding *o*-diphenylbenzene to phenylcyclohexane solutions of durene. The durene radiation is already completely quenched by small amounts of *o*-diphenylbenzene. If the energy in the pure solvent could go to the *o*-diphenylbenzene by radiation and then from the *o*-diphenylbenzene by radiation to another substance, there should be a large decrease in intensity. The experiment with fluoranthene, however, shows only a slight decrease in intensity which can be understood only by energy transfer from the solvent itself and not by radiation. To draw the energy from *o*-diphenylbenzene, a larger concentration of fluoranthene is needed because the lifetime of the excitation energy in the *o*-diphenylbenzene molecule is shorter than in the molecule of the initial solvent. If the energy transfer should occur via radia-

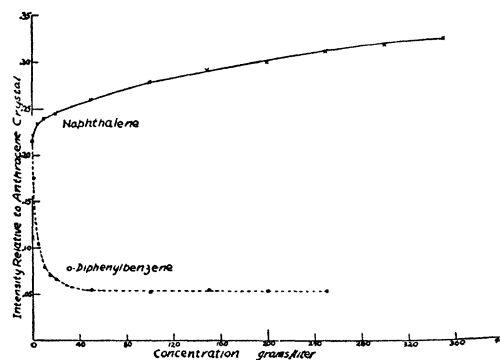


FIG. 8. Effect of naphthalene and *o*-diphenylbenzene on xylene + diphenylhexatriene (1 g/l).

tion, the increased concentration of fluoranthene would not accelerate the transfer from *o*-diphenylbenzene to fluoranthene.

E. SUMMARY

The experiments with naphthalene and *o*-diphenylbenzene solutions seem to us to provide proof for our ideas on energy transfer and the method of adding fluorescent molecules to such solutions appears to make it possible to localize the excitation energy. The fact that these solutions have practically no radiation of their own, but can, nevertheless, still produce considerable light emission with some other fluorescent molecules can be looked upon as a support for our ideas in connection with the mechanism of energy transfer in fluorescent solutions. In particular, they demonstrate that only those fluorescent molecules with an emission spectrum of larger λ than that of the transferring molecule show the phenomenon of increased light emission when the solvent is irradiated by γ -radiation. They further indicate the importance of the quenching factor τ_q for the maximum intensity and the maximum concentration, and show that τ_q for the solvent, and τ_i for the solute have the same physical significance of internal quenching. Finally, they also demonstrate the importance of the self-quenching mechanism on the emitted light intensity.

It was found that three types of fluorescent materials can be distinguished in mixed solutions containing an "additional solute," such as naphthalene or *o*-diphenylbenzene, producing only a small light emission of their own. The *first* type has emission and absorption spectra of shorter wavelengths than most of the absorption spectrum of the additional solutes. The fluorescence of these materials is strongly decreased by very small amounts of the additional solute as a consequence of the absorption of the fluorescent light by these molecules and its internal quenching. Durene is an example of this type of fluorescent molecule if naphthalene or *o*-diphenylbenzene is added. The *second* type of fluorescent material has absorption and emission spectra close to those of the additional solute. The light emission of these fluorescent molecules is strongly decreased by larger amounts of the additional solute. This decrease in radiation is not due to absorption but results from the fact that the additional solute draws energy from the bulk material, and that this energy is then no longer available for energy transfer to the fluorescent molecule owing to the difficulty of trapping. Terphenyl

and *m*-diphenylbenzene are molecules of this type. The *third* type of fluorescent molecule has an emission spectrum consisting of considerably longer wavelengths than those of the additional solutes. As a consequence they can also draw excitation energy from the additional solutes and then trap this energy if the concentration of the additional solute is comparable or higher than that of the fluorescent molecule. In this case the energy transfer occurs in two steps. First, an energy transfer occurs from the original solvent to the additional solute molecules and then from these molecules to the fluorescent molecules. In this sense the additional solute acts in some way as a second solvent. The intensity of the fluorescent light depends strongly on the internal quenching of the additional solute. Anthranilic acid and diphenylhexatriene belong to this group of substances when naphthalene or *o*-diphenylbenzene is added.

Similar effects may also occur in all mixed solutions if the additional solutes emit considerable light by themselves. In these cases, however, the special effects mentioned above are masked by the comparatively strong light emission of the additional solutes.

This article deals with the mechanism of energy transfer in fluorescent materials. In this connection, however, some other concepts are disclosed by these measurements which may be of some interest. One in particular is that these measurements show that the differences in light emission from various fluorescent molecules is not so much due to a change in the probability of light emission, $1/\tau_e$, but is mostly affected by a change in the internal quenching $1/\tau_i$. This internal quenching probability is very sensitive to structural changes in the molecules as can be seen from the comparative measurements with *p*-, *m*-, and *o*-diphenylbenzene, all of which have approximately the same absorption and emission spectra (the *o*-diphenylbenzene emission was not obtained). In these cases the change in the configuration of the three benzene rings produces changes in the quenching probability by an order of magnitude. The measurements also show that this probability is dependent on the solvent.⁸ Some of the variations in different solvents stem from this influence on the internal quenching probability. The measurements with naphthalene and *o*-diphenylbenzene indicate that the internal energy transfer is by no means limited to fluorescent molecules but generally also with non-fluorescent molecules.

⁸ E. J. Bowen and A. Norton, *Trans. Faraday Soc.* **35**, 44 (1939).

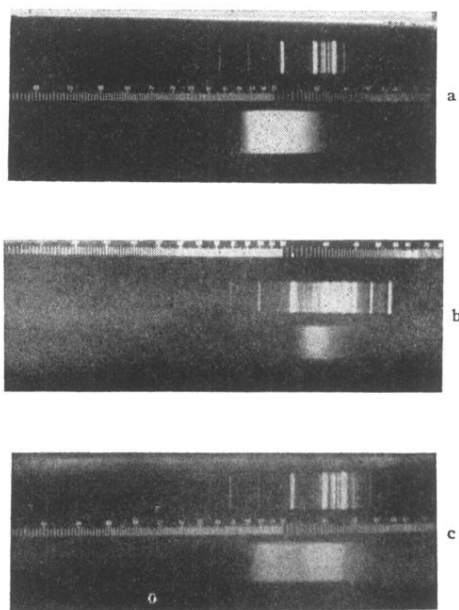


FIG. 3. (a) Terphenyl solution. (b) Terphenyl solution +0.1 g/l anthranilic acid. (c) Terphenyl solution+trace of diphenylhexatriene.