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Enhancement of Fluorescence in Solutions Under High-Energy Irradiation*

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Organic solutions with poor high-energy-induced fluorescence can often be made much more efficient by introducing large concentrations of substances such as naphthalene and some related compounds. The naphthalene can be considered as an intermediate solvent; the energy originally mainly absorbed in the less effective solvent goes over to the naphthalene from which it then proceeds to the fluorescent solute. Naphlene is considerably more effective as such an intermediate solvent than any other of the known efficient solvents, e.g., xylene. It is shown that the particular effectiveness of naphthalene stems from two causes: first, the energy transfer from the "poor" solvent to naphthalene is faster than to other substances; secondly, the excited naphthalene molecule is often quenched less than, e.g., xylene by quenching atoms present in the solution. These results are applied to the enhancement of the high-energy-induced fluorescence of solutions containing various elements even as heavy as bismuth.

IN recent work,[1] it was shown that the absence of considerable high-energy-induced fluorescence in some solutions is due to a lack of energy transfer from the solvent to the fluorescent molecule, most likely as a consequence of the very short lifetime of the excited solvent molecule. Another effect frequently impeding high-energy-induced fluorescence is that some molecules, especially those of a "poor" solvent, often have the property of quenching other excited molecules, both of the solvent and solute, thereby reducing the high-energy- (and light)-induced fluorescence. It was found that quenching of this latter type more often affects excited solvent molecules than those of the solute.

The purpose of this paper is to show that substances exist which, when put into poorly fluorescent solutions in sizeable amounts, enhance the fluorescence to a greater extent than does the introduction of the known most efficient solvents. Naphthalene and some related compounds can be employed in this manner and are considerably more effective than xylene.

The effectiveness of these substances as intermediate solvents may be due to two processes: First, a more efficient energy transfer occurs from the "poor" solvent to naphthalene than, for example, to xylene. Secondly, the excited naphthalene molecules undergo a smaller quenching (in many instances) by surrounding molecules than do the excited molecules of other substances. The quenching of the excited solvent molecule by the addition of special molecules is often more prominent than that of the solute molecule and is demonstrated by some examples as follows:

High-energy fluorescence is often strongly reduced by the presence of oxygen.[2,3] Thus if the fluorescence is determined as a function of the solute concentration (for example in solutions of xylene and terphenyl), the addition of oxygen is found to produce a shift in the maximum of the curve of fluorescence *vs* concentration toward larger solute concentrations, and similarly the removal of oxygen results in a shift of the maximum toward lower concentrations. The maximum light intensity, however, is changed comparatively little by the removal of oxygen, indicating that mainly the solvent rather than the solute molecule is quenched by oxygen.[4]

Another example is tetralin which, though a very "effective" solvent when pure, deteriorates (from the fluorescence point of view) upon standing in air. This deterioration decreases the high-energy-induced fluorescence tremendously but only comparatively slightly influences the light-induced fluorescence, for example, of 9,10-diphenylanthracene. This shows that the decrease of fluorescence in such tetralin solutions occurs because of quenching of the excited solvent molecules rather than those of the solute.[4]

A final illustration is presented by nitric acid molecules which produce strong quenching of the high-energy fluorescence of xylene or phenylcyclohexane solutions. It is again found that the quenching acts most strongly upon the excited solvent molecule, and the replacement of xylene by naphthalene results in a considerable improvement of the high-energy-induced fluorescence.

EXPERIMENTAL RESULTS

The experiments described below were performed with the same arrangement as that described in a previous paper by the authors[5] except that a nonreflecting beaker was used. Integrated intensity measurements were made, and the high-energy excitation source was 1 mC radium.

The particular effect of naphthalene is demonstrated in Figs. 1 to 4. *n*-butylphosphate was used as the basic solvent; it is very stable and little deterioration of the fluorescence of suitable solutes with time is found. Considerable quantities of many organic substances of

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[1] M. Furst and H. Kallmann, Phys. Rev. (to be published).

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

[3] Pringle, Black, Funt, and Sobering, Phys. Rev. **92**, 1582 (1953).

[4] This will be discussed more fully in a forthcoming paper.

[5] H. Kallmann and M. Furst, Phys. Rev. **79**, 857 (1950).

interest for high-energy fluorescence can be dissolved in it. This solvent by itself, however, displays only small high-energy fluorescence with most of the well-known fluorescent solutes in the usual moderate concentrations.

Figure 1 presents the gamma-ray-induced fluorescence of solutions in *n*-butylphosphate with two different concentrations of 2,5-diphenyloxazole as a function of additional xylene and naphthalene. It is seen that for both solute concentrations the naphthalene curve is above the xylene curve by a factor 1.5. This is interpreted as being due to a faster energy transfer from the *n*-butylphosphate to naphthalene than to xylene when equal masses of naphthalene and xylene are added, since there is no difference in energy transfer from naphthalene or xylene respectively to the solute as shown below. If the fluorescent intensities are compared when equal numbers of molecules are added to the original solvent (instead of equal masses), the difference is even more favorable for naphthalene. It is unfortunate that the naphthalene curve cannot be obtained for high concentrations; only about 23 percent of the solution can consist of naphthalene at room temperature. If the fluorescence of 2,5-diphenyloxazole in pure naphthalene could be determined, the intensity would probably be the same and not higher than that in pure xylene. This conclusion can be deduced from the result that the addition of naphthalene to xylene does not noticeably alter the fluorescence although it is known that with sufficient naphthalene the energy is first transferred from xylene to naphthalene and then finally to the solute.[6] If this conclusion is correct, the curves for xylene and naphthalene of Fig. 1 would merge for 100 percent xylene and naphthalene.

Figure 2 describes similar experiments, this time with a fixed concentration of 9,10-diphenylanthracene serving as the light emitting solute and various amounts of different additional "solvents." Again it can be seen that added naphthalene is more effective than xylene. Acenaphthene behaves very much the same as naphthalene; its own fluorescence is larger than that of naphthalene, but it is still small when compared to that produced by the 9,10-diphenylanthracene. α,α'-binaphthyl gives a much larger fluorescence than naphthalene; in this case the energy is transferred to diphenylanthracene by absorption of radiation as well as by collision, and this makes the fluorescence curve higher. The effect of absorption is noticeable because of the small concentration of diphenylanthracene, which is only slightly soluble. These measurements show that the energy transfer to naphthalene and to related compounds is very similar. The energy transfer to *m*-diethoxybenzene has also been measured in order to study the behavior of a substance which is a moderately effective solvent (as a pure solvent it is about half as effective as xylene). In *n*-butylphosphate it is again about half as good as xylene, indicating that the energy transfer from *n*-butylphosphate to this substance is of the same order as to xylene.

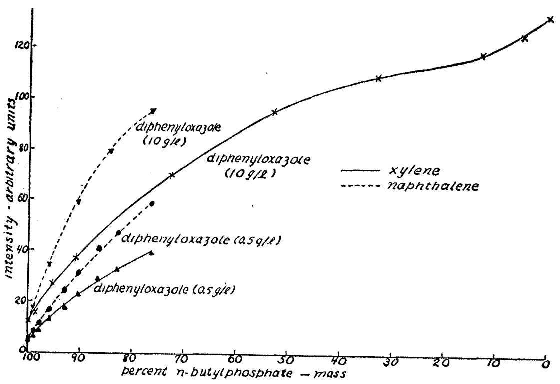

FIG. 1. Florescence of 2,5-diphenyloxazole in mixtures with *n*-butylphosphate.

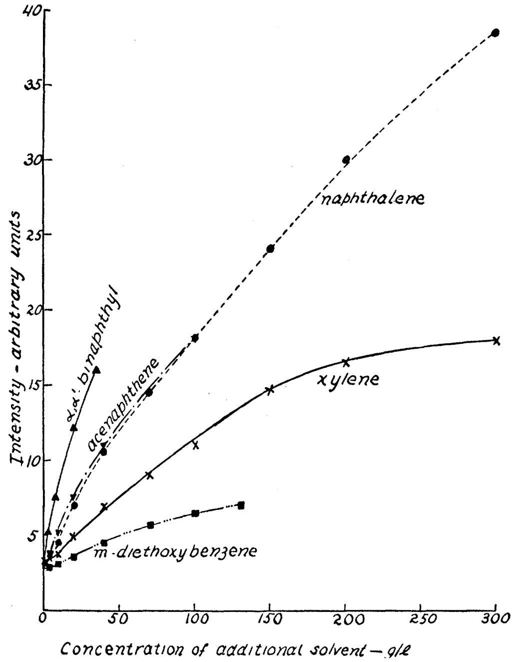

FIG. 2. Effects of additional "solvents" on *n*-butylphosphate +9,10-diphenylanthracene (0.5 g/l).

Comparison of these results with those obtained from the addition of naphthalene to a solution of *p*-terphenyl in xylene[5] reveals that the lifetime of the excited solvent molecule is shorter in *n*-butylphosphate than it is in xylene; this is seen from the better energy transfer to naphthalene in solutions made with xylene than in those with *n*-butylphosphate. Thus when 10 g/l of naphthalene are added to a terphenyl-xylene solution a decrease in fluorescence by a factor of more than three is found.[6] In a solution of 2,5-diphenyloxazole in *n*-butylphosphate, however, the addition of 10 g/l of naphthalene produces only a small increase as can be seen

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[6] M. Furst and H. Kallmann, Phys. Rev. **94**, 503 (1954).

in Fig. 1. In the terphenyl-xylene solutions most of the energy originally in the xylene proceeds to the naphthalene with only 10 g/l; but it cannot then go to the terphenyl because of the close proximity of the energy levels of naphthalene and terphenyl; thus the observed large decrease in light output occurs. In *n*-butylphosphate, however, with the same amount of naphthalene only a small fluorescence change occurs because of the poorer transfer of energy to the naphthalene due to the shorter lifetime of the excited butylphosphate molecule. Only when larger amounts of naphthalene are present can this effect of shorter lifetime be overcome. It is interesting to note that the fluorescence of the highest available naphthalene concentration is only about 25 percent below the maximum fluorescence in solutions with pure xylene. This shows that the energy transfer process from *n*-butylphosphate to naphthalene does not involve much loss of energy, which is in agreement with the contention made earlier.

Figure 3 presents the fluorescent light output as a function of the 2,5-diphenyloxazole concentration for various amounts of xylene and naphthalene in *n*-butylphosphate. For the maximum naphthalene concentration (~23 percent of solution by mass), the intensity is already 75 percent of that of a 100 percent xylene solution. Since 25 percent of the primary energy is directly absorbed in the naphthalene, it is calculated from the preceding result that about 70 percent of the energy directly absorbed in *n*-butylphosphate is transferred to the naphthalene at these concentrations whereas with xylene only about 50 percent is transferred. This conclusion is drawn since measurements with light-induced fluorescence have shown that the addition of naphthalene or xylene does not change the light output and thus the internal quenching of such a solute, and since the curves of fluorescence *vs* concentration for naphthalene and xylene respectively in *n*-butylphosphate have the same forms. These curves display shifts of the optimum concentration toward higher concentrations when compared to the curve of 2,5-diphenyloxazole in xylene. This can be interpreted as stemming from a shorter lifetime (due to a stronger quenching) of the excited naphthalene or xylene molecules by surrounding *n*-butylphosphate molecules than without this substance being present. Such an increase of quenching reduces the true lifetimes of these excited molecules thereby decreasing the energy transfer probability to the solute; the result of the shortening of lifetime is a shift in the maximum of the fluorescence *vs* concentration curve. Such stronger quenching by the addition of *n*-butylphosphate to xylene can also be seen from the xylene curve of Fig. 1. There the drop in fluorescence occurring when small amounts of *n*-butylphosphate are added to xylene is probably due to this quenching. One must also consider that some energy transfer still takes place directly from *n*-butylphosphate to the solute; this increases with greater 2,5-diphenyloxazole concentration. Its contribution, however, is still too small in the case of 300 g/l of naphthalene or xylene to account for the observed shift in the curve; with only 50 g/l of naphthalene present this process does become important and partially accounts for the different shape of the corresponding curve. The forms of the 300 g/l naphthalene curve and that of the respective xylene curve, however, are so similar to each other that no difference in lifetime between the excited xylene and excited naphthalene molecules (i.e., in energy transfer from these molecules to the solute) is indicated under these conditions where the *n*-butylphosphate quenching is relatively small.

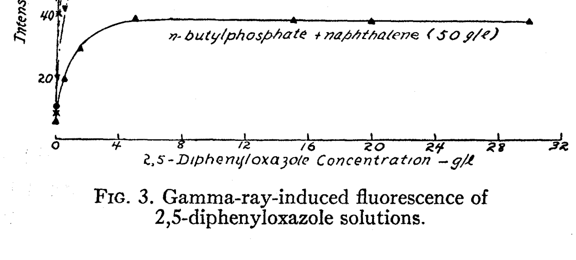

FIG. 3. Gamma-ray-induced fluorescence of 2,5-diphenyloxazole solutions.

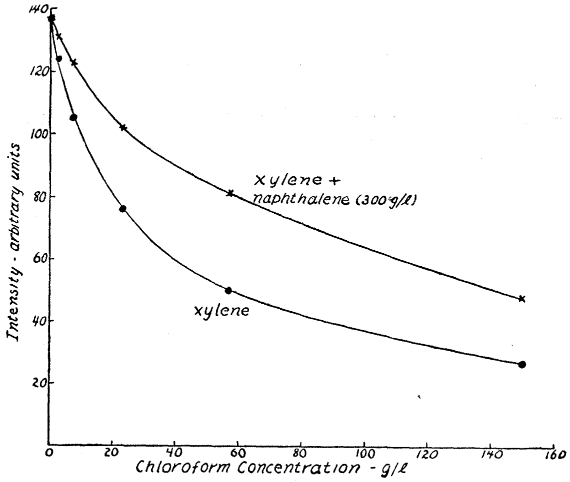

FIG. 4. Effect of chloroform on solutions with 2,5-diphenyloxazole (5 g/l).

Such a difference is, however, indicated in other cases in which strong quenching by the surrounding molecules occurs and becomes quite evident from the experiments described in Fig. 4. Here the quenching influence of chloroform on γ-ray-induced fluorescence is studied in solutions of 2,5-diphenyloxazole in pure xylene and in xylene plus 300 g/l naphthalene; in the latter case the

Table I. γ-ray fluorescence of solutions containing various elements.

Elements	Solution "Solvent"[a]	Fluorescent solute	Percent of intensity of the same solute in xylene
Boron	Trimethylborate	2,5-diphenyloxazole (3 g/l)	5
	Trimethylborate 50%+xylene 50%	2,5-diphenyloxazole (3 g/l)	79
	Trimethylborate 47%+xylene 31% +naphthalene 22%	2,5-diphenyloxazole (3 g/l)	95
Silicon	Tetraethylorthosilicate	α-naphthylphenyloxazole (3 g/l)	5
	Tetraethylorthosilicate 75% +naphthalene 25%	α-naphthylphenyloxazole (3 g/l)	74
Phosphorous	*n*-Butylphosphate	2,5-diphenyloxazole (10 g/l)	9
	n-Butylphosphate 70%+naphthalene 30%	2,5-diphenyloxazole (10 g/l)	72
Sulfur	Phenylcyclohexane 47%+thiophene 53%	9,10-diphenylanthracene (20 g/l)	28[b]
	Phenylcyclohexane 43%+thiophene 48% +naphthalene 9%	9,10-diphenylanthracene (20 g/l)	61[b]
Chlorine	Chloroform 15%+xylene 85%	2,5-diphenyloxazole (4.5 g/l)	20
	Chloroform 14%+xylene 64% +naphthalene 22%	2,5-diphenyloxazole (4.5 g/l)	35
Arsenic	Xylene 96%+triphenylarsine 4%	9,10-diphenylanthracene (10 g/l)	42
	Xylene 86.5%+triphenylarsine 3.5% +naphthalene 10%	9,10-diphenylanthracene (10 g/l)	83
	Xylene 81%+triphenylarsine 9.5% +naphthalene 9.5%	9,10-diphenylanthracene (10 g/l)	58
Antimony	Xylene+triphenylstibine 1%	9,10-diphenylanthracene (2 g/l)	34
	Xylene 87%+naphthalene 12% +triphenylstibine 1%	9,10-diphenylanthracene (2 g/l)	81
	Xylene 81%+naphthalene 16% +triphenylstibine 3%	9,10-diphenylanthracene (2 g/l)	57
Mercury	Xylene 90%+di-*n*-butylmercury 10%	α-naphthylphenyloxazole (5 g/l)	9
	Xylene 69%+di-*n*-butylmercury 10% +di-*n*-butylmercury 7%	α-naphthylphenyloxazole (5 g/l)	18
	Xylene 66%+naphthalene 23% +di-*n*-butylmercury 11%	α-naphthylphenyloxazole (5 g/l)	15
Lead	Tetraethyllead 10%+xylene 90%	9,10-diphenylanthracene (10 g/l)	24
	Tetraethyllead 9%+xylene 81.5% +naphthalene 9.5%	9,10-diphenylanthracene (10 g/l)	39
	Tetraethyllead 42.5%+xylene 42.5% +naphthalene 15%	9,10-diphenylanthracene (10 g/l)	15
Bismuth	Xylene+triphenylbismuthene 2.5%	α-naphthylphenyloxazole (3 g/l)	25
	Xylene 73%+naphthalene 25% +triphenylbismuthene 2%	α-naphthylphenyloxazole (3 g/l)	54
	Xylene 70%+naphthalene 24% +triphenylbismuthene 6%	α-naphthylphenyloxazole (3 g/l)	21

[a] The percentages indicated are of mass.

[b] In phenylcyclohexane rather than xylene.

energy transfer to the fluorescent solute takes place from the naphthalene molecules. The influence of chloroform on the diphenyloxazole molecule does not differ in the two solutions. Now it is seen that the quenching in the xylene plus naphthalene solution is smaller than in the solution with xylene alone throughout the entire range of chloroform concentrations including small concentrations. Energy transfer from the "poor" solvent (chloroform), especially at low chloroform concentrations, produces little interference and therefore does not conceal the actual quenching process. The difference between the two "solvents" is due to the difference in quenching of the excited molecules of xylene and naphthalene respectively; the naphthalene molecule is therefore considered to be quenched less by chloroform than the xylene molecule in agreement with the previous results. These results provide a verification of the statements made in the introductory paragraphs.

Results with naphthalene similar to those described above in *n*-butylphosphate are also obtained with other "poor" solvents and quenchers; some examples can be seen in Table I.

APPLICATIONS

For many experiments, especially in the field of nuclear physics, it is desirable for specific elements (or more complicated substances) to be present in a scintillating material. Frequently, however, the substance by itself has only poor fluorescent properties under high-energy radiation, and when it is put into an efficient fluorescent solution a considerable decrease in light output results because of quenching. Such behavior is often found when materials contain elements of medium or heavy atomic weights. By applying the results obtained with added naphthalene, solutions which exhibit considerable fluorescence have been made with such quenching molecules present.

A list of substances containing different elements is presented in Table I with which at least moderate high-energy fluorescence efficiencies can be obtained in organic liquid solutions. (The common elements in organic substances such as hydrogen, carbon, nitrogen, and oxygen are not included.) In most cases, as can be seen from the table, the addition of large amounts of naphthalene produces sizeable enhancement of the light output although considerable amounts of the quenching material may be present in the solution. The various fluorescent solutes shown in the table give comparable results, and in many cases α,α'-binaphthyl may also be used. *p*-terphenyl cannot be utilized because of the insufficient energy transfer found with naphthalene.[6] The heaviest element that has been successfully used to the present has been bismuth. The list which is presented represents the results of a preliminary search for successful substances. Finding substances with desirable properties presents certain problems. One of the major difficulties is the lack of solubility in suitable organic solvents. Once a soluble material is found, it must generally be such that it does not quench the solution too strongly. The naphthalene, as discussed above, acts as a "solvent" in which less quenching occurs and provides a medium to and from which more energy is transferred.

The investigation presented in this paper opens up the possibility of studying the influence of various atoms and molecules on other excited molecules not normally present in work with fluorescence.

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Energy Levels of a Disordered Alloy

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A study is made of the one-electron energy levels of a disordered alloy by means of perturbation theory, extending the results of Nordheim and Muto. To the accuracy of first-order perturbation theory, a disordered alloy is equivalent to a particular perfect crystal, the "virtual crystal," as was shown by Muto. For a certain rather general model, the effects of second-, third-, and fourth-order perturbation theory upon this "virtual-crystal" approximation are analyzed. The question of convergence of the perturbation approach is studied. A certain basic limitation of the perturbation approach is discussed, namely, the limitation to nonlocalized states. Accurate results obtained by Landauer and Helland for a hypothetical one-dimensional alloy are compared with results obtained by perturbation theory. It is pointed out that the same approach can be used with equal validity in discussing not only disordered alloys but also other types of imperfect crystals; e.g., imperfections resulting from dislocations. The most striking prediction of perturbation theory, i.e., the "tailing-off" of the density-of-states curve into a forbidden band, appears to have some experimental verification.

I. INTRODUCTION

IN this paper we will discuss the one-electron energy levels of a completely disordered alloy. For hypothetical one-dimensional alloys, this problem has recently been solved with the aid of computing machines.[1,2] For the three-dimensional problem, however, there seems to be little hope of a reasonably exact solution. The great difficulty, over and above the problem of a perfect crystal, lies in the lack of spacial periodicity of the disordered alloy even though the atoms of the alloy may reasonably be assumed to lie on periodic lattice sites. For this reason, we will attempt to solve the problem by perturbation theory. Such an approach was used by Muto[3] in an attempt to justify Nordheim's "virtual-crystal" approximation.[4] This approximation consists of replacing the correct one-electron potential (appropriate to a given configuration of atoms of the alloy) by its average (the average to be taken over all possible random configurations). In order to gain some physical insight into the accuracy of the approximation, we will now rephrase Muto's discussion in terms of electron scattering in the alloy.

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