

CONCENTRATION QUENCHING OF LIQUID SCINTILLATORS

M. FURST and H. KALLMANN

*Physics Department, New York University**

MOST of us who work in this field are familiar with the usual variations in fluorescence intensity with concentration in a single solute solution. Under high energy excitation when the concentration of the solute is increased, there is first an increase in intensity to a maximum and then eventually a decrease. This paper is concerned with this decrease which is usually called self or concentration quenching.

The elementary processes that are responsible for this effect are not accurately known. One might think that the self quenching of the excited molecules is connected with their lifetime; this, however, is not corroborated by all experiments. Something that is known however is that when the molecules are less mobile, for instance in polystyrene, the self-quenching is decreased. It is generally assumed that concentration quenching occurs between like molecules, one of which is excited and one of which is not excited. This presentation deals with the question of the extent of 'likeness' necessary for self-quenching.

The basic method used for studying this is by determining the behavior of solutions containing two solutes which have rather similar fluorescence but different chemical structures. There are several choices, or one might think there are, in relation to the mode of excitation. One might first try using light excitation where the incoming light is absorbed by the solute. It is then often difficult to excite both solutes to approximately the same degree because of great differences in absorption of the different compounds. High energy excitation, however, using appropriate solvents like xylene or *p*-dioxane avoids this difficulty since transfer occurs from the solvent to the solute, and this transfer is essentially proportional to the relative masses of the solutes. Therefore, if equal masses of solute are used, equal excitation is obtained. Consequently this work was done with gamma ray excitation. We have also tried light, but where the solvent absorbed the incoming light. As Dr. Kallmann showed in his talk, similar results as under gamma-ray excitation are obtained, but when high concentrations are used, there is difficulty because of direct solute absorption.

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There is also a possibility of employing light excitation where the absorption edges of the solutes differ. The irradiation is then done using a wavelength where one of the solutes absorbs and the other does not. In this way the effect of one solute molecule on the other can be studied. Some preliminary work on this has been done which corroborates findings under high energy excitation.

For a single solute, it is found that the intensity as function of concentration, is rather well represented by the formula

$$I = \frac{Pc}{(Q+c)(R+c)} \quad (1)$$

In this formula $1/Q$ is related to the ability to transfer energy from the solvent to the solute, and the P and R values are both related to self-quenching. Now for two solutes in solution there are some complications. For instance the excited light intensity depends on absorption and emission spectra of the solutes. For instance if the emission from one of the solutes considerably overlaps the absorption range of the other solute, then there is the difficulty that internal quenching may overwhelm the self-quenching effects which are being studied. In order to get around this, solutes are required which have about the same emission region.

First, some of the theoretical formulas considering two solutes will be given. Equation (2) gives the light emission for two solutes in solution which do not interact from the self quenching standpoint (no cross quenching), and equation (3) gives the intensity when such cross quenching occurs.

$$I = \frac{Qc}{(Q+c)} \left[\frac{P_1}{Q_1 \left(\frac{R_1}{f} + c \right)} + \frac{P_2}{Q_2 \left(\frac{R_2}{1-f} + c \right)} \right]$$

$$\text{where } Q \equiv \left[\frac{f}{Q_1} + \frac{1-f}{Q_2} \right]^{-1} \quad (2)$$

$$I = \frac{cQ}{(Q+c)} \left\{ \frac{P_1 f}{\left[f + \frac{\beta_{12}}{\beta_{11}} (1-f) \right] \left[\frac{R_1}{f + \frac{\beta_{12}}{\beta_{11}} (1-f)} + c \right] Q_1} + \frac{P_2 (1-f)}{\left[1-f + \frac{\beta_{21}}{\beta_{22}} f \right] \left[\frac{R_2}{1-f + \frac{\beta_{21}}{\beta_{22}} f} + c \right] Q_2} \right\} \quad (3)$$

I is the emitted intensity and c is the total solute concentration, that is the concentration of both solutes and f is the solute fraction made up by solute

1. All of the parameters are related to the single solute parameters P_i , Q_i , R_i of the single solute solution. There are no adjustable parameters in equation (2); the predicted intensity follows directly from the single parameter results. An overall reduction in quenching compared to that of the single solutes occurs. In equation (3) the cross quenching is given essentially by β_{12} and β_{21} and the individual quenchings by β_{11} and β_{22} . There are difficulties in studying the coefficients β_{12} and β_{21} in equation (3) which respectively give the cross quenching produced in solute 2 by solute 1 and vice versa. These parameters can be obtained only in experiments such as the ones reported here, and therefore equation (3) cannot be independently verified. The other self quenching parameters β_{11} and β_{22} can be obtained independently of these cross quenching experiments with the aid of emission and absorption curves. However, if interaction occurs, then the formula for non-interaction (equation (2)) does not hold very well. This is the criterion which is used to determine whether cross quenching occurs to a sizeable extent.

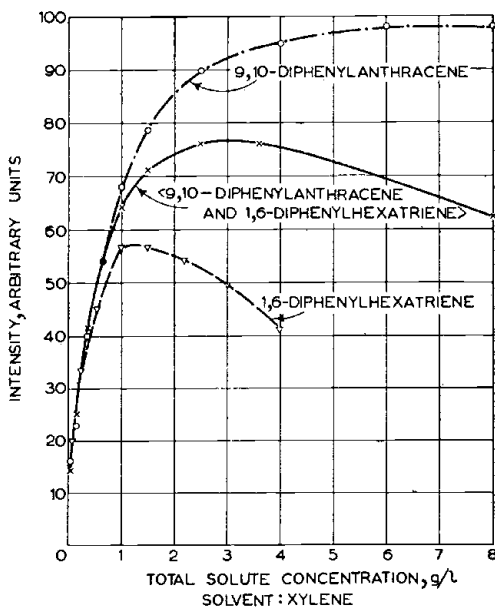


Fig. 1. Gamma-ray induced fluorescence in xylene solutions of 9,10-diphenylanthracene, of 1,6-diphenylhexatriene, and of half and half combinations (mass) of the two.

The first experimental results presented show some cases where no interaction is expected to occur because of great differences in the structure of the molecules. The concentrations on the graphs are always total solute concentrations. From the single solute curves one can see (Fig. 1) that 1,6-diphenylhexatriene exhibits strong self-quenching whereas 9,10-diphenylanthracene

has medium self-quenching. Before applying the formulas, it should be pointed out that Q_1 and Q_2 are usually about the same order of magnitude. Equation (2) then shows that if the two solutes do not interact, there is a shift of the maximum intensity toward higher concentration. Also one expects, especially at large concentrations, that the intensity is greater than that of the substance when alone in solution which shows the larger self-quenching. From the figure one can notice that this certainly occurs which would seem to indicate non-interaction.

Now consider the results predicted by equation (2) which are given in Table I. At the bottom the parameters are given for each single solute and for the combination. Looking at the table, there is considerable deviation at low

TABLE I
Gamma-ray Induced Fluorescence of Xylene Solutions of Half and Half Combination (Mass) of 1,6-Diphenylhexatriene and 9,10-Diphenylanthracene

Concentration g/l.	Intensity	
	Observed	Calculated
0.01	9.7	2
0.05	14.5	8
0.15	25	21
0.35	41	39
0.65	54	56
1	64	67
1.5	71	75
2.5	76	80
3.6	76	81
8	62	75

$$\text{1,6-diphenylhexatriene } I = \frac{305c}{(0.8+c)(2+c)}$$

$$\text{9,10-diphenylanthracene } I = \frac{8400c}{(0.8+c)(70+c)}$$

$$\text{Combination } I = \frac{0.8c}{(0.8+c)} \left[\frac{305}{0.8(4+c)} + \frac{8400}{0.8(140+c)} \right]$$

concentrations between the actual and predicted results. This effect also occurs with single solute solutions and is due to the neglect of the effect of pure solvent radiation. This effect is certainly negligible in efficient solvents at concentrations of about 1 g/l. Again it may be pointed out that there are no adjustable parameters. There is good agreement with equation (2) at medium concentrations. At high concentrations, there is some deviation. Whether this effect was due to absorption was checked by use of solutions having smaller depths. Absorption effects were found to be negligible. The conclusion is that

there is little cross quenching, but as indicated from the observed deviation from equation (2), some does exist.

The next experimental results (Fig. 2) are also for solutes which are not expected to interact, but each separately has high self-quenching. 1,6-diphenylhexatriene and also fluorescent chartreuse are used; the latter is a

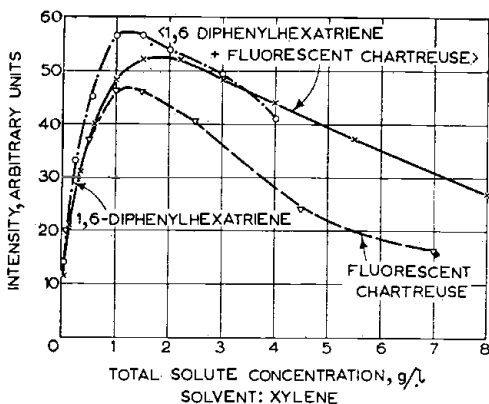


Fig. 2. Gamma-ray induced fluorescence in xylene solutions of 1,6-diphenylhexatriene, of fluorescent chartreuse, and of half and half combinations (mass) of the two.

commercial substance, the exact structure of which we do not know, but it is probably a diaminostilbene. The reason that fluorescent chartreuse has been chosen is that its self-quenching is about the highest found. Examining the curves one sees the shift in the maximum intensity concentration. Here each single maximum occurs at about the same concentration, and the combined curve shows considerable shift to the right. Also notice that the intensity of the combined solute curve exceeds that of either single curve at high concentrations. This is predicted by the non-interaction formula. This greater intensity occurs despite the existence of sizeable absorption by the fluorescent chartreuse of the diphenylhexatriene radiation.

Considering the calculated values which are listed in Table 2, one can see that they are considerably higher than the observed. However multiplying by a constant factor determined to give equal intensity at the concentration of maximum observed intensity gives good agreement except at low concentrations because of solvent radiation effects which were previously mentioned. The reason for multiplying by this factor is that the diphenylhexatriene radiation is absorbed to a certain extent by the other solute. This has been checked by measurements on solutions of different depths. The effect of absorption is essentially of decreasing the actual amount of emitted radiation. Absorption, however, will not change the essential shape of the curve, and therefore the absorption can be taken care of by multiplying with a constant factor. The

agreement after multiplying by a constant factor shows that there is no cross quenching between these different molecules although each separately exhibits considerable self-quenching.

Now more closely related compounds were studied with the anticipation that strong interaction would occur although the molecules are not identical.

TABLE 2

Gamma-ray Induced Fluorescence of Xylene Solutions of Half and Half Combination (Mass) of 1,6-Diphenylhexatriene and Fluorescent Chartreuse

Concentration g/l.	Intensity		
	Observed	Calculated	Calculated $\times 0.79^*$
0.01	9	2	1.6
0.05	11.5	9	7
0.15	21	24	19
0.35	31	43	34
0.6	40	55	44
1	48	64	51
1.5	52	67	53
2.2	52	65	51
3	48	63	50
4	44	55	44
5.5	37	47	37
8	27	38	30

$$\text{1,6-diphenylhexatriene } I = \frac{305c}{(0.8+c)(2+c)}$$

$$\text{fluorescent chartreuse } I = \frac{165c}{(0.9+c)(0.9+c)}$$

$$\text{combination } I = \frac{0.85c}{(0.85+c)} \left[\frac{305}{0.8(4+c)} + \frac{165}{0.9(1.8+c)} \right]$$

* The values calculated from the combination formula are multiplied by a constant in order to take account of losses most likely due to absorption by the chartreuse of the diphenylhexatriene radiation.

Anthracene and some of its derivatives were chosen because of their spectral characteristics and considerable quenching. Figures 3 and 4 are examples to point out what happened in such cases. In particular the fluorescence of solutions of anthracene and 9-methylanthracene and solutions of anthracene and 2-methylanthracene were measured. Figure 3 with 9-methylanthracene shows that there is a shift in concentration of maximum intensity in the double solute solution compared to either alone. Also at higher concentrations the intensity in the double solute solution rises above either single curve. These results show that this is a case of little or no cross quenching.

Calculated values, which are not shown here indicate a fair fit with the non-interaction formula. Multiplication by a constant factor is necessary because some absorption occurs. Thus even in this case there is little interaction.

Consider now similar solutions made with 2-methylanthracene (Fig. 4). Here as can be seen there is no shift of the concentration of maximum intensity. However, there is an indication that a slight cross-over occurs at high concentrations. These results show that interaction does occur so that from the quenching point of view anthracene and 2-methylanthracene are similar

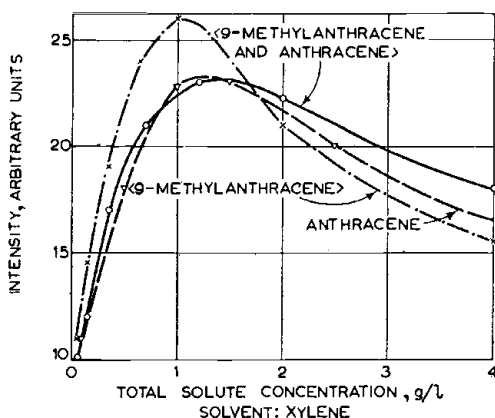


Fig. 3. Gamma-ray induced fluorescence in xylene solutions of anthracene, of 9-methylanthracene, and of half and half combinations (mass) of the two.

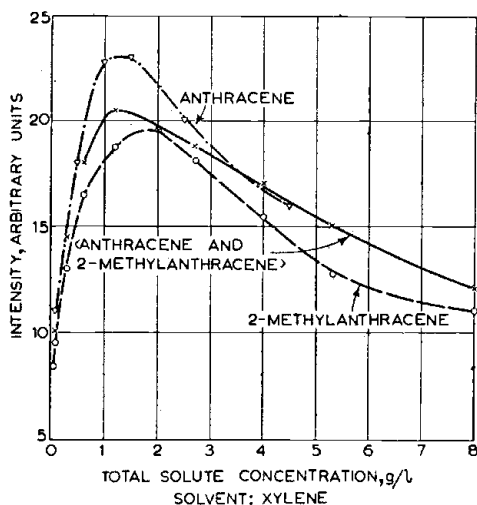


Fig. 4. Gamma-ray induced fluorescence in xylene solutions of anthracene, of 2-methylanthracene, and of half and half combinations (mass) of the two.

molecules. The results shown in Table 3 corroborate this. The position of the maximum does not match very well; there is considerable shift, and multiplying by a constant factor does not produce agreement. This is then a case of genuine cross-quenching between different molecules. It is interesting to conjecture on why these anthracene derivatives behave so differently.

TABLE 3

Gamma-ray Induced Fluorescence of Xylene Solutions of Half and Half (Mass) of Anthracene and 2-Methylantracene

Concentration g/l.	Intensity		
	Observed	Calculated	Calculated $\times 0.78$
0.05	8	3	2
0.1	10	6	4
0.3	15	3	10
0.6	18	20	15
1.2	21	26	21
2	20	26	21
2.7	19	25	20
4	17	24	19
5.3	15	22	17
8	12	19	15

$$\text{2-methylantracene } I = \frac{148c}{(0.85 + c)(3.4 + c)}$$

$$\text{anthracene } I = \frac{127c}{(0.8 + c)(2.1 + c)}$$

$$\text{Combination } I = \frac{c(0.82)}{(0.82 + c)} \left[\frac{148}{0.85(6.8 + c)} + \frac{127}{0.8(4.2 + c)} \right]$$

It is well known chemically that 9- and 10-positions of anthracene have greater reactivity than the other positions. Thus when you have 9-methylantracene, the molecule is essentially different from anthracene, and these two molecules do not interact from the quenching point of view. Another idea concerns the actual geometrical configuration of the molecules. The 9-substitution is in the middle whereas the other is at the side. It is possible that in the 2-substitution, the molecules can get closer to each other than they can with the 9-position substitution.

To corroborate these findings, since 9-methylantracene does not interact with anthracene whereas 2-methylantracene does interact with anthracene, the fluorescence of a combination of 2-methylantracene and 9-methylantracene was measured; and it was found there was no interaction in agreement with the previous result. It is concluded from the experiments that

2-methylanthracene is 'like' anthracene whereas 9-methylanthracene is 'different'. A number of other combinations which there is no time to go into here have also been tried. To mention two examples: For instance, 1,4-diphenylanthracene and 9,10-diphenylanthracene show no interaction whereas 9,10-di-*p*-tolylanthracene and 9,10-di-*m*-tolylanthracene appear to interact.

In conclusion, it may be stated that some more complete studies of this type may help to reveal some of the mechanisms of self-quenching. Studies like this also open up the possibility of studying dimer like configurations where there are different molecules instead of the same molecule, one of which is excited. So far our results seem to show that considerable cross quenching occurs only when the molecules have similar energies of excitation and when they are closely related structurally. They do not have to be identical.