effect. The rapid decrease of electron plasma temperature and population of excited atoms during arc-current interruption offer an explanation for the short extinguishing time of cold-cathode arcs. The similarities between the D type of arc and the mercury pool arc suggest that excited atoms play a predominant role in the emission mechanism of low-boiling-point metal arcs.

Cross Quenching of Fluoresence in Organic Solutions*

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Concentration quenching is usually considered to occur only between excited and unexcited molecules of the same kind. It is here investigated whether such quenching may also occur between molecules of different structure. Equations are given for testing its occurrence. By using gamma-ray induced fluorescence of solutions containing a combination of two solutes, it is found that concentration quenching occurs between molecules of different structure if their energy levels are close to each other.

I. INTRODUCTION

THE fluorescence output under light or high-energy excitation of a single solute solution measured as a function of solute concentration first increases and eventually decreases with increasing concentration at large enough concentrations; this decrease is brought about by concentration (or self) quenching.[1-3] The answer to the question of which elementary process is primarily responsible for this quenching is not yet definitely known although many mechanisms have been proposed. All of these mechanisms have the common assumption that in an encounter between an excited and an unexcited molecule of the same kind a resonance interaction becomes effective which may be attractive or repulsive. This interaction either decreases the emission probability of the molecule (if the lowest state of the two molecules together is less radiative) or it may increase the quenching probability (by bringing the respective molecules closer to each other). Which of these processes is the more important has not yet been ascertained, but in any case it is generally assumed that such a quenching process occurs only between molecules of the same kind. There is the question of whether only identical molecules give rise to the concentration quenching interaction. Does this interaction occur, for example, with molecules which differ from each other only in the position of various groups within a molecule? It is noteworthy in this respect that

compounds having related structures and only slight differences in absorption and emission spectra may have large differences in self-quenching, e.g., anthracene and 9,10-diphenylanthracene. The concentration quenching of the latter is about 30 times less than the former. Compounds like anthracene and 2-methylanthracene, on the other hand, exhibit a similar amount of concentration quenching.

It might be expected that concentration quenching and lifetimes of the molecules in solution are correlated, if one conjectures for instance that this quenching is brought about by a resonance interaction proportional to the emission probability per unit time. This probability is proportional to the area under the extinction coefficient curve (as a function of wavelength) in the wavelength region corresponding to the lowest excited electronic energy state; this is proportional to the transition dipole moment responsible for the resonance interaction. Another possibility, just the reverse of the previous, is that concentration quenching is inversely related to the lifetime of the molecule since longer lived molecules have a greater chance for quenching encounters. Neither surmise agrees with experimental evidence obtained from a large number of substances investigated in this laboratory. Consider again, for example, anthracene and 9,10-diphenylanthracene. Anthracene in solution possesses one of the shortest lifetimes but also very large concentration quenching and 9,10-diphenylanthracene has a long lifetime and small concentration quenching. Thus the reasons for large differences in concentration quenching have not yet been determined. There is, however, one result which is consistently found in experiments: it is the decrease of concentration quenching when the mole-

[1] Peter Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1949); also contains an extensive bibliography.
[2] H. Kallmann and M. Furst, Phys. Rev. **79**, 857 (1950).
[3] M. Furst and H. Kallmann, Phys. Rev. **85**, 816 (1952).

cules are less mobile; as an example, solutions in polystyrene (plastic) show little or no quenching. This paper deals mainly with the question of the degree of "sameness" which is necessary for concentration quenching.

2. EXPERIMENTAL METHOD

The problem is attacked by measuring the fluorescence of solutions containing two solutes of related fluorescent properties and comparing the fluorescence with that of solutions containing each solute by itself. If light excitation is used and the solutes are directly excited, there is often difficulty because of a considerable difference in absorption strength of the substances at a given wavelength. In such a case equal numbers of excited molecules of both types can be obtained only by having different concentrations of each molecule in the solution; but then the actual concentration quenching of the substances is quite different because of the concentration differences, even when each substance alone displays a similar degree of concentration quenching. On the other hand, when high-energy radiation is used to excite the solutions, it is found that energy transfer from solvent to solute depends essentially on the relative masses of the dissolved solutes when a solvent suitable for energy transfer like xylene or p-dioxane is used, and thus a uniform distribution of excitation between the two types of molecules is easily obtained. Light excitation may be used instead if wavelengths predominantly exciting the solvent molecules are employed. These light excitation experiments, however, are more limited than those under high-energy excitation because absorption by the solute in many cases becomes noticeable at rather moderate concentrations. Consequently this study has so far been carried out with high-energy excitation. Light could also be used advantageously to excite one of the solutes when a difference in absorption edges of the solutes exists. In this case the exciting wavelengths should be in the region where only one of the solutes absorbs. The effect of the nonabsorbing solute on the fluorescence of the absorbing solute can then be studied, but again this can work only in a rather limited number of cases. However, experiments of this type are contemplated.

3. THEORETICAL CONSIDERATIONS

In many solutions containing a single solute under excitation by high energy, the fluorescence intensity, I, as a function of solute concentration c has been shown[2,3] to be well represented by an expression of the form:

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

The parameter Q is inversely related to energy transfer from solvent to solute, and P and R depend inversely on concentration quenching of the solute. When two

solutes are present, the behavior depends greatly on the absorption and emission spectra of the solutes. If emission from one of the solutes lies within the absorption region of the other, the light output from the solution is in the region of the latter solute at concentrations usually employed. The effects of internal quenching[3] in the finally emitting solute very often overwhelm those due to concentration quenching. In order to study cross quenching between different solutes when the energy is transferred from the solvent, it is thus necessary to use solutes which do not match in these spectra to any sizable extent. This is perhaps most conveniently assured by investigating substances both of which emit in approximately the same spectral region.

In solutions containing two such solutes the high-energy induced fluorescence light output I as a function of total (both solutes) solute concentration, $c=c_1+c_2$, is calculated basically as in references 2 and 3, and results in formula (2) for the particular case where the solutes do not mutually interact in the manner of concentration quenching.

$$I = \frac{cQ}{(Q+c)} \left[\frac{P_1}{Q_1[(R_1/f)+c]} + \frac{P_2}{Q_2[R_2/(1-f)+c]} \right]. \quad (2)$$

Here f is the fraction of the total solute comprising solute 1, and the other parameters relate to the behavior when each solute is present alone in the same solvent, and $Q \equiv [f/Q_1 + (1-f)/Q_2]^{-1}$. Experiments have shown that energy transfer is the same for most fluorescent solutes so that the parameters Q_1 and Q_2 are usually nearly equal. If no interaction occurs, the overall effect is a reduced quenching. Thus, for two non-interacting substances of identical fluorescence, the maximum emission occurs at a greater total concentration than that found using either solute alone, and the fluorescence decreases more slowly at high concentrations than does that of the single solute.

When the two solutes are "similar," by which it is meant that they interact from the concentration quenching point of view, then the following more complicated expression results:

$$I = \frac{cQ}{(Q+c)}$$

$$\times \left\{ \frac{P_1 f}{[f+(\beta_{12}/\beta_{11})(1-f)]\left[\dfrac{R_1}{f+(\beta_{12}/\beta_{11})(1-f)}+c\right]Q_1} \right.$$

$$\left. + \frac{P_2(1-f)}{[1-f+(\beta_{21}/\beta_{22})f]\left[\dfrac{R_2}{1-f+(\beta_{21}/\beta_{22})f}+c\right]Q_2} \right\}. \quad (3)$$

All parameters have the same meaning as in (2); β_{ij} is a measure of the cross quenching produced on an ex-
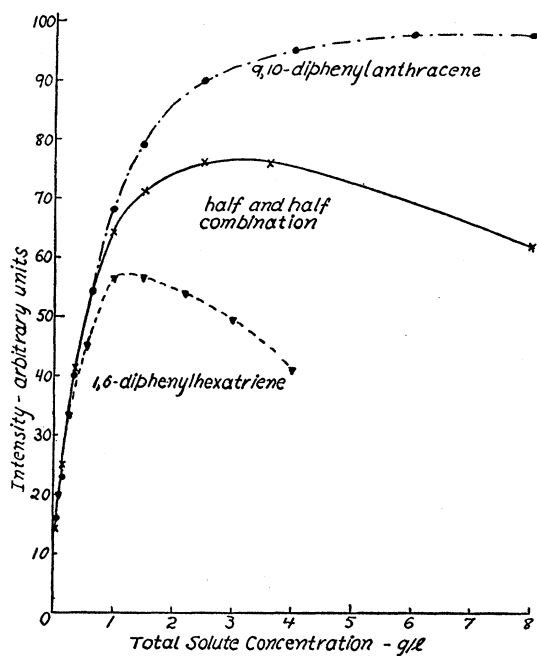
FIG. 1. Gamma-ray-induced fluorescence in xylene solutions of 9,10-diphenylanthracene, of 1,6-diphenylhexatriene and of half and half (mass) of the two.
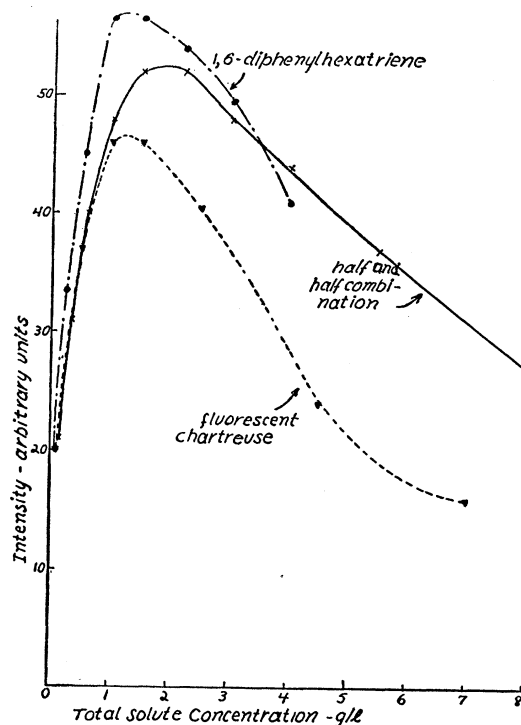

FIG. 2. Gamma-ray-induced fluorescence in xylene solutions of 1,6-diphenylhexatriene, of fluorescent chartreuse and of half and half (mass) of the two.

cited molecule of type i because of interaction with an unexcited molecule of type j. In the limit when the two substances are "identical," the cross quenching is that of either substance. The parameters β_{11} and β_{22} are a measure for concentration quenching between two molecules of type 1 and type 2, respectively. They are defined in the following way: $\beta_{11}c_1$ is the probability per unit time of concentration quenching. Normally they occur in the R factor $[R = 1/\tau\beta_{11}]$ where τ is the mean life of the excited solute molecule when there is no concentration quenching. β_{11} and β_{22} can be determined from these lifetimes and the R values. The cross quenching parameters β_{12} and β_{21} however can only be obtained from experiments similar to those described here. From (3) it follows that the over-all quenching is greater when cross quenching is present than that in (2). A check of whether cross quenching occurs can be carried out by comparing (2) with experimental results. If (2) provides a good representation of the measurements, this quenching does not occur.

4. EXPERIMENTAL RESULTS

Results of experiments are given in Fig. 1 to Fig. 4 and in Tables I to IV. The first two figures and tables show the behavior of substances which might not be expected to interact from a concentration quenching point of view. Both of these figures and especially Fig. 2 show that there is little cross quenching in these instances since the curve of the combined solutes displays much less decrease in light output at high concentration than expected with cross quenching, and

there is a shift in position of maximum intensity to higher concentration. In Fig. 2 there is even a crossing over at large concentrations by the curve of the combination of solutes above that of the higher intensity substance (1,6-diphenylhexatriene), and the maximum of the combination curve occurs at higher concentrations than those of the curves of the two substances

TABLE I. Gamma-ray-induced fluorescence of xylene solutions of half and half (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

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

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

Combination $\quad I = \dfrac{0.8c}{(0.8+c)}\left[\dfrac{305}{0.8(4+c)} + \dfrac{8400}{0.8(140+c)}\right]$
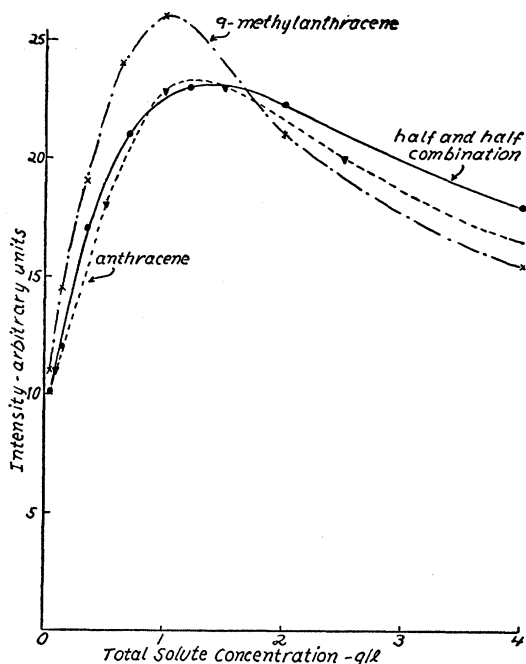
FIG. 3. Gamma-ray-induced fluorescence in xylene solutions of anthracene, of 9-methylanthracene and of half and half (mass) of the two.
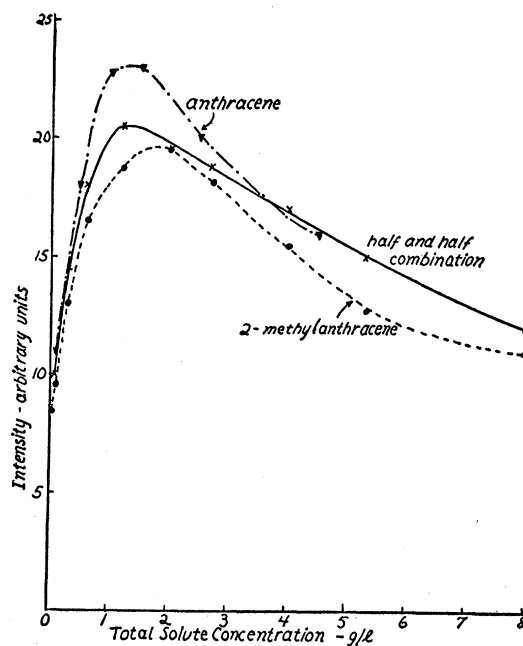

FIG. 4. Gamma-ray-induced fluorescence in xylene solutions of anthracene, of 2-methylanthracene and of half and half (mass) of the two.

alone despite the high concentration quenching of the individual solutes.

It can be seen from Table I that the results experimentally obtained when 1,6-diphenylhexatriene and 9,10-diphenylanthracene are in combination are not badly represented by Eq. (2) using parameters obtained when the solutes are used singly in the same

TABLE II. Gamma-ray-induced fluorescence of xylene solutions of half and half (mass) of 1,6-diphenylhexatriene and fluorescent chartreuse.

Concentration g/l	Intensity Observed	Intensity Calculated	Calculated ×0.79[a]
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	50.5
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

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

Fluorescent chartreuse $I = \dfrac{165c}{(0.9+c)(0.9+c)}$

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

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

solvent. The observed decrease in light emission as a function of concentration is more rapid than predicted by Eq. (2) at high concentrations, indicating that small cross quenching does occur. This will be discussed further below. The poor agreement of observed and calculated results at low concentrations is due to emission from the solvent (which is considered negligible in the theory) and the smallness of the solute emission. In comparing the calculation with the experimental results, it must be borne in mind that the calculated curves are based on the parameters from the single compounds.

The interpretation of Fig. 2 is somewhat different. The combination of 1,6-diphenylhexatriene and fluorescent chartreuse is particularly interesting since these substances singly in solution exhibit nearly the largest concentration quenching found among all substances.[4] Equation (2) is a fairly good representation for the shape of the experimental curve indicating that cross quenching between the two substances is quite small although each substance alone shows strong concentration quenching. However its absolute values are too high; multiplication of the calculated intensities by the factor 0.79 gives rather good agreement. Equation (2) contains no adjustable parameter. Now fluorescent chartreuse has an absorption spectrum somewhat more extended to the visible than that of diphenylhexatriene. Thus a portion of the fluorescence emitted by diphenylhexatriene is absorbed by the other substance and is

[4] Furst, Kallmann, and Brown, J. Chem. Phys. 26, 1321 (1957).

TABLE III. Gamma-ray-induced fluorescence of xylene solutions of half and half (mass) of 9-methylanthracene and anthracene.

Concentration g/l	Intensity		Calculated ×0.74
	Observed	Calculated	
0.01	9	0.9	0.7
0.05	10	4.1	3
0.15	12	10.8	8
0.35	17	19.7	14.5
0.7	21	27.4	20.2
1.2	23	31.3	23
2	22	31.3	23
4	18	26.3	19.3

Anthracene $\quad I=\dfrac{127c}{(0.8+c)(2.1+c)}$

9-methlyanthracene $\quad I=\dfrac{102c}{(0.9+c)(1.1+c)}$

Combination $\quad I=\dfrac{c(0.85)}{(0.85+c)}\left[\dfrac{127}{0.8(4.2+c)}+\dfrac{102}{0.9(2.2+c)}\right]$

then re-emitted. There is a certain loss in light output since the efficiency of fluorescent chartreuse is not unity especially at large concentrations. The necessity of multiplying by a constant does not affect the conclusion that cross concentration quenching does not occur since other processes such as absorption or energy transfer would tend to make the decrease in light output at large concentrations greater than that found.

In order to clarify the situation, the influence of absorption has been more thoroughly studied. It may be emphasized that in these experiments only a (small) portion of the emission spectrum of one substance overlaps the absorption spectrum of the other. Since absorption and re-emission are associated with a loss, a lower light output results. This effect might be thought to explain the larger theoretical values compared to experiment in the case discussed in Table I. This hypothesis was tested by repeating that experiment with a solution depth one tenth as great as before. Except

TABLE IV. Gamma-ray-induced fluorescence of xylene solutions of half and half (mass) of anthracene and 2-methylanthracene.

Concentration g/l	Intensity		Calculated ×0.78
	Observed	Calculated	
0.05	8.3	3	2.3
0.1	10	5.5	4.3
0.3	15	13.2	10.3
0.6	18	19.8	15.5
1.2	20	26.2	20.5
2	20	26.4	20.6
2.7	19	25.5	20
4	17	24.2	19
5.3	15	22	17.2
8	12	18.5	14.5

2-methylanthracene $\quad I=\dfrac{148c}{(0.85+c)(3.4+c)}$

Anthracene $\quad I=\dfrac{127c}{(0.8+c)(2.1+c)}$

Combination $\quad I=\dfrac{c(0.825)}{(0.825+c)}\left[\dfrac{148}{0.85(6.8+c)}+\dfrac{127}{0.8(4.2+c)}\right]$

for the decrease in absolute values no appreciable change in shape was found. When the experiments of the type depicted in Fig. 2 were carried out at smaller depths there was also no change in shape compared to large depths, but the multiplication factor was larger (0.85) and therefore closer to unity as expected if absorption occurs. It may appear peculiar that the effect of absorption shows up as a constant multiplicative factor rather than a decrease in emission at high concentration. The explanation is that at medium concentrations the part of the light which can be absorbed is already practically completely absorbed, and increase in concentration does not change the percentage absorbed appreciably. There is a rather sharp drop in absorption coefficient with increasing wavelengths. It is also possible that energy can go over via "collision," but this is not connected with a noticeable loss since the efficiency of each substance is about the same.

In the solution containing diphenylhexatriene and diphenylanthracene there is an interaction between the two solute molecules. This interaction could be explained by the assumption that energy transfer by "collision" occurs from diphenylanthracene to diphenylhexatriene. Since diphenylhexatriene has a smaller light-emitting efficiency, this would make the experimental curve lie below the calculated as is found. Measurements of the absorption characteristics of these substances, however, show that this cannot occur since the energy level of diphenylhexatriene is greater than that of diphenylanthracene. The interaction is also not one due to absorption effects (shown by experiments at different depths). It is therefore inferred that there is a concentration quenching interaction between diphenylanthracene and diphenylhexatriene although it is small. Its occurrence may be associated with the closeness in energy levels of these two materials so that interaction due to temperature effects is possible.

The behavior when substances more closely related structurally as well as in fluorescent properties are in solution is shown in Figs. 3 and 4 and in Tables III and IV. An examination of the curves reveals a decided difference in behavior of the solutions in these cases. Here again, as in Fig. 2, the solutes used singly have rather similar characteristics. The intensity maximum of the solutions containing anthracene and 9-methylanthracene occurs at a higher concentration than that of either solute used singly. This is a feature which occurs when concentration quenching interation between different molecules is small. Also the behavior at high concentrations, where the double solute fluorescence is greater than either alone, indicates that there is little if any interaction between the molecules. Absorption by the 9-methylanthracene of anthracene radiation may account for the fact that the maximum of the combination curve is somewhat low similarly as for the substances shown in Fig. 2, but this does not alter the shape of the curve. Upon multiplying with a

constant, the calculated values from Eq. (2) agree rather well with experiment as is seen in Table III. The 2-methylanthracene anthracene solution, however, does not exhibit a shift of its maximum to a concentration greater than that of the single solute solutions. This indicates that considerable cross quenching interaction between the different types of molecules occurs; this interaction is, however, not so strong as that between identical molecules. This is borne out by the fact that the combination curve eventually appears to cross the curves of both single solutes. Table IV shows that the shape of this curve is not well represented by Eq. (2). The decrease in emission at high concentrations is too great; also energy transfer does not influence these curves appreciably. This is an instance of genuine cross quenching between two similar but not identical substances.

In addition a number of other combinations of anthracene derivatives, and other combinations have been measured. Generally it was found that the over-all quenching is reduced when there are two solutes. Considerable cross quenching has been found to occur only when the compounds are closely related structurally.

5. CONCLUSIONS

The experiments show that concentration (cross) quenching occurs between nonidentical molecules especially when their absorption and emission spectra and their fluorescent properties are fairly similar. Thus anthracene and 2-methylanthracene exhibit mutual concentration quenching to a rather high degree whereas such cross quenching is already much less between anthracene and 9-methylanthracene. This is not unexpected since the 9 and 10 positions are the most reactive ones in anthracene. It is thus understandable that a substitution in the 9 position produces a more significant change in behavior than a similar one in the 2 position. The shape of the molecule may also be of importance for the interaction. Substances with similar absorption and emission spectra but different structures show only small cross quenching. From a theoretical viewpoint, it is understandable that closely related but not identical substances exhibit cross quenching. Self-quenching is not a process which occurs with large collision cross sections. On the contrary, from the concentration at which self-quenching occurs, one computes a quite normal (geometrical) or even smaller cross section. Thus, to bring about a cross quenching, a very exact resonance is not required. Probably it is sufficient that the difference between the energy levels concerned is of the order of thermal energies, and this can occur with similar but not identical molecules.

Studies of this type present the possibility of investigating dimer-like configurations of nonidentical molecules, one of which is excited.