

26. *Solvent Quenching of Fluorescence.*

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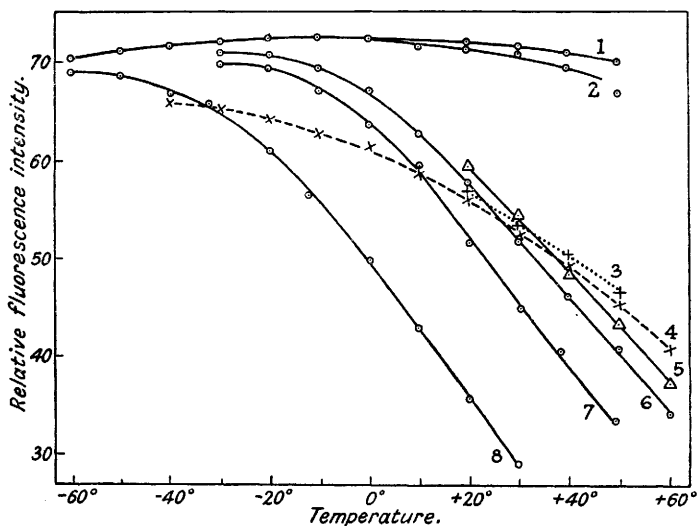
Experiments are described of the effect of temperature on the fluorescence of solutions of rubrene, naphthacene, and anthracene in various solvents. It is concluded that "dispersion force" complexes play an important part in fluorescence quenching, and that when they are

of long life they act as "inner filters"; this effect differing from other types of quenching by its negative temperature coefficient.

THIS paper describes experiments on the effect of temperature on the fluorescence of solutions of aromatic hydrocarbons in various solvents, made with the aim of throwing light on the problem of quenching by solvent molecules.

The apparatus used consisted of a small, clear Dewar vessel to contain the solution, with an internal closed metal tube for the reception of heating or cooling devices. Below this tube a concentrated, filtered beam of exciting light passed through the liquid, and at right angles to this direction the fluorescence, after passing another filter, was measured by means of a potassium photo-cell with electrometer-valve amplification. It was found that for a light absorption of about 20% the observed fluorescence was a maximum and practically independent of concentration, owing to the rise of total fluorescence with increasing concentration being balanced by the geometric factors of the proportion of the fluorescent light collected by the photo-cell. This occurred at concentrations of about 0.03 g./l., well below those where effects of concentration quenching are evident. All experiments were carried out at this concentration.

FIG. 1.



Fluorescence of solutions of rubrene, 0.03 g./l.

- | | |
|--------------------|------------------------|
| 1. In cyclohexane. | 5. In dioxan. |
| 2. In n-hexane. | 6. In n-butyl alcohol. |
| 3. In benzene. | 7. In ethyl alcohol. |
| 4. In toluene. | 8. In acetone. |

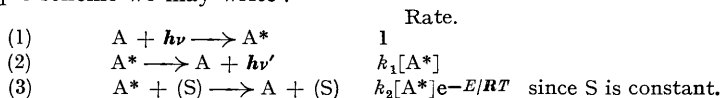
As fluorescent hydrocarbons, rubrene, naphthacene, and anthracene were used with the following light sources and filters:

Hydro-carbon.	Light source, filter, and wave-length.	Filter for fluorescence.
Rubrene	Filament projection lamp with 1 cm. of satd. $\text{Cu}(\text{NO}_3)_2$; 4700—5400 Å.	Iford 201
Naphthacene	Mercury lamp with ammoniacal CuSO_4 and acidified ferric alum filters; 4050 and 4360 Å.	Iford 108
Anthracene	Mercury lamp with Chance's OX glass; 3650 Å.	Iford 805

The solutions were cooled with liquid oxygen and heated by a nichrome spiral in the metal tube, stirring and oxygen removal being performed by a fine stream of dry hydrogen or nitrogen. Dry air was caused to circulate over the outside of the Dewar vessel to prevent moisture condensing at low temperatures.

Fig. 1 shows the results for solutions of rubrene in various solvents. It is apparent that in hexane and *cyclohexane* the fluorescence varies little over the temperature range, and there is reason to think that the actual efficiency is near unity (Bowen and Norton, *Trans. Faraday*

Soc., 1939, **35**, 44). In the other solvents the fluorescence diminishes as the temperature is raised. As a simple scheme we may write:



where E is the heat of activation of the quenching process.

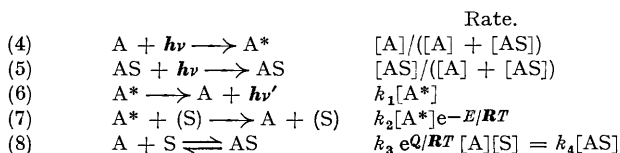
If F_0 represents the fluorescence without and F the fluorescence with quenching, then

$$\log_{10} (F_0 - F)/F = \log_{10} k_2/k_1 - E/2.3RT$$

Using the data of Fig. 1, we obtain

Solvent.	log ₁₀ k_2/k_1 .	E (k.-cals./mole).	Solvent.	log ₁₀ k_2/k_1 .	E (k.-cals./mole).
Acetone	4.7	6.46	<i>n</i> -Butyl alcohol ...	4.7	7.15
Alcohol	4.74	6.94	Dioxan	4.72	7.28

The fluorescence in these solvents tends to the hexane value at low temperatures. This is not so, however, for the solvents benzene and toluene, where the limiting value is less and the curves fall off less steeply with temperature. These flat aromatic molecules probably form "dispersion force" van der Waals complexes of unusual stability with the fluorescent molecules (see Bowen, "The Chemical Aspects of Light", 2nd edition, Clarendon Press, 1946, p. 167). These complexes are less stable than those with nitro-compounds (Briegleb, *Z. physikal. Chem.*, 1936, **32**, 305) or dye polymers (Vickerstaff and Lemin, *Nature*, 1946, **157**, 373) and affect the extinction coefficients of the solution only slightly, but we may assume that the absorbed light is divided between free and combined fluorescent molecules and that only the former fluoresce. The reaction scheme as so modified is:



Whence $F_0/F = (1 + k_3 e^{Q/RT}/k_4)(1 + k_2 e^{-E/RT}/k_1)$.

The terms of the expression vary in opposite senses with temperature, and at low temperatures F_0/F does not rise to unity.

Experiments on naphthacene show the likelihood of this explanation. Naphthacene is a very insoluble hydrocarbon and its fluorescence could not be measured over a wide temperature range.

Fig. 2 shows results for the fluorescence of naphthacene in several solvents, including xylene with additions of 40 g./l. of naphthalene, diphenyl, and benzophenone. The effect of these added flat aromatic molecules on the fluorescence is qualitatively just as would be expected on the hypothesis of the formation of non- or feebly fluorescent complexes. A similar effect of these substances on the fluorescence of rubrene was also observed (cf. Sambursky and Wolfsohn, *Nature*, 1946, **157**, 228).

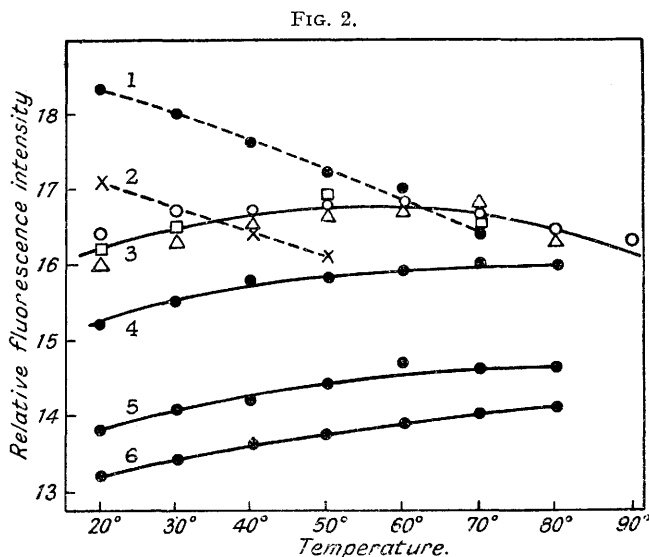
The influence of van der Waals forces on quenching is shown by the fluorescence of rubrene in mixtures of chloroform and acetone as depicted in Fig. 3. This pair of liquids is well known to give a minimum in the vapour pressure-composition curve. The minimum is due to the geometry of these molecules whereby they fit together closely so that van der Waals forces are more satisfied than in either of the pure components. There is thus less van der Waals force left over for the solute rubrene in the mixture, and, as expected, the fluorescence curves show maxima, more marked the lower the temperature.

From the results of experiments on the fluorescence of rubrene in hexane, with additions of toluene as quencher, values of k_3 were obtained for van der Waals quenching by toluene. These are of the order of 0.012 and, allowing for this, the values of E and log₁₀ k_2/k_1 for toluene solutions of rubrene are in good agreement with those for other solvents: $E = 7.62$ k.-cals./mole; log₁₀ $k_2/k_1 = 4.7$.

The fluorescence efficiency of naphthacene solutions is very low, probably about 0.1, and internal quenching processes besides "solvent quenching" are probably operative.

The fluorescence efficiency of anthracene solutions is also less than unity (*Trans. Faraday*

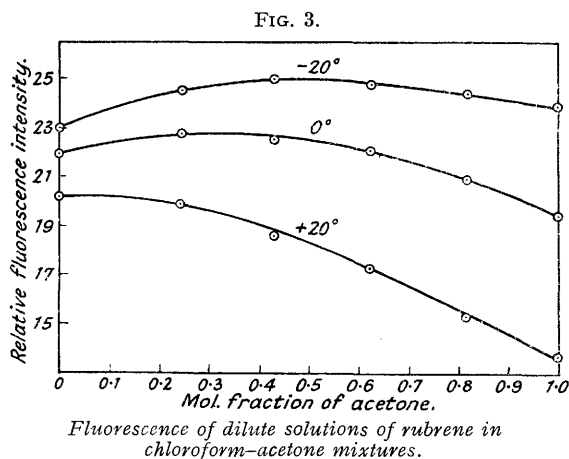
Soc., 1937, **33**, 1425; 1939, **35**, 765) and some experiments were made on the effect of temperature. In benzene solution the fluorescence falls off above ordinary temperatures while in toluene it is almost temperature-independent even to low temperatures. Evidently the com-



Fluorescence of solutions of naphthacene, 0.03 g./l.

1. In xylene-ethyl alcohol mixture, 50% by vol.
2. In xylene-acetone mixture, 50% by vol.
3. \circ In xylene; \square in benzene; \triangle in toluene.
4. In xylene containing diphenyl, 40 g./l.
5. In xylene containing benzophenone, 40 g./l.
6. In xylene containing naphthalene, 40 g./l.

plexes are less readily dissociated by heat in the latter solvent. The fluorescence in hexane solution increases at low temperatures, and this must be due to other effects than "solvent quenching" of the type discussed above.



and may be affected by solvent both by its differential effect on the curves and by changes in the probability of the molecule passing over from one curve to the other. External quenching is the removal of energy by collision. Both may have an energy of activation as shown in reactions (3) and (7) above. Where the solvent itself may possibly act as a quencher it is not easy to distinguish between these two possibilities. However, the difference between them may not be so sharp as might appear. Both may be translated into terms

The measurements described above indicate that a distinction must be drawn between quenching effects due to interaction of solvent or solute molecules and the fluorescent molecule *before* or *after* the latter have absorbed a light quantum. In the former case the quenching is of the nature of an "inner filter" effect of the complexes formed between molecules in their ground states. The light absorbed by the complex is degraded either by conversion to vibrational or translational energy, or by chemical reaction. In the second case there are two possibilities, "internal" or "external". Internal quenching arises from a crossing of the potential-energy curves of the excited and ground levels of the fluorescent molecule,

based on the hypothesis of complex formation; on the internal mechanism the complex represents the effect of solvent on the fluorescent molecule, and on the external one complex formation and collision can be related. Fluorescence quenching in liquid systems must therefore be treated rather differently from quenching in gaseous systems.

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