

Solvent Quenching of the Fluorescence of Anthracene.

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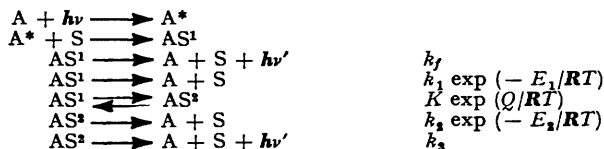
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The effect of temperature on the fluorescence efficiency of anthracene in a number of solvents has been measured. The changes observed are interpreted in terms of Mulliken-type interactions between excited solute and solvent molecules involving an element of A-S⁺ structure.

THE effect of temperature on the fluorescence of solutions is still imperfectly understood. Rise of temperature may decrease or increase fluorescence intensity, and effects which are independent of concentration may be interpreted as van der Waals interactions with the solvent of the fluorescent molecules in either their ground or their excited states (Bowen and Coates, *J.*, 1947, 105; Bowen and Cook, *J.*, 1953, 3059). Measurements are here described relating to anthracene dissolved in several organic solvents, made over a wider range of temperature than so far recorded. The solutions were contained in small Dewar vessels, illuminated by 3650 Å radiation at one side, and the fluorescence measured at 90°. They were de-oxygenated and stirred by a fine stream of nitrogen and heated or cooled by a dipping copper rod along which heat was conducted when its upper end was either heated electrically or cooled with liquid oxygen. Temperatures were measured by a dipping thermocouple. The anthracene concentrations were about 10⁻⁴M, and fixed at the point where the geometry of the apparatus gave a maximum measurable intensity. No great change in light absorption or band shape occurs over the temperature range studied, so that measurements could be directly converted into absolute quantum efficiencies by using the value of 0.24 for deoxygenated benzene solutions at ordinary temperature (Bowen and Williams, *Trans. Faraday Soc.*, 1939, 35, 765).

The Figure shows graphically the variation of anthracene fluorescence with temperature for a number of solvents.* The curves show positive and negative temperature coefficients; toluene and *p*-xylene give maxima. Mixtures of solvents of opposite temperature coefficients also produce maxima (Bowen and Cook, *loc. cit.*). This lends support to the hypothesis that solvent quenching is a complex effect depending on the different positions of an excited solute molecule in the solvent cage and on detailed van der Waals interactions between different parts of the molecules.

Recent work on the fluorescence of phenols (Förster, *Z. Elektrochem.*, 1950, 54, 42, 531; Mataga, Kaibe, and Korzumi, *Nature*, 1955, 175, 721) has shown that the excited states are more acidic than the ground states, and that equilibration of excited states in van der Waals interaction with the solvent is rapid compared with the rate of fluorescence emission. If it is assumed that equilibration is also rapid for aromatic hydrocarbons, Bowen and Cook's kinetic scheme (*loc. cit.*) may be modified as follows:



where AS¹ and AS² are two rapidly interchanging modes of interaction of excited solute and solvent.

This scheme gives the fluorescence efficiency F equal to:

$$\frac{1}{(1 + k_a e^{-E_1/RT})(1 + Ke^{Q/RT})} + \frac{Ke^{Q/RT}}{(1 + k_b e^{-E_2/RT})(1 + Ke^{Q/RT})}$$

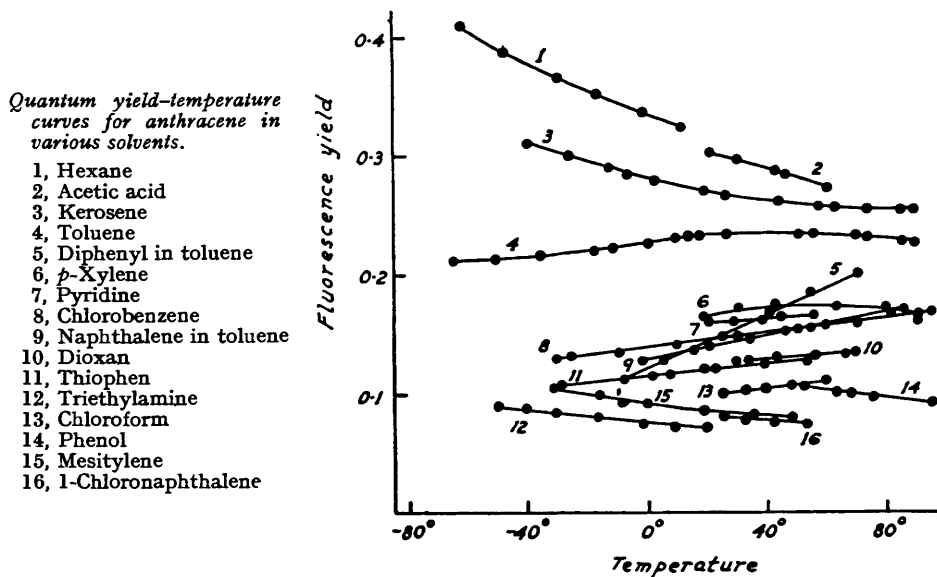
* In Tables 1 and 2 of Bowen and Cook (*loc. cit.*) the expression $F_0(1 - 10^{-4}\alpha t)$ should be corrected to $F_0 - 10^{-4}\alpha t$.

where $k_1/k_f = k_a$ and $k_2/k_3 = k_b$. The assumption of $K = 0$ leads to the equation

$$\log_{10} (1/F - 1) = \log_{10} k_a - E_1/4.6T$$

Even for hexane solutions this simplified equation is not obeyed over the range of temperature studied.

There are too many unknown constants in the general equation to apply it fully to existing data, and its derivation is necessarily of a crude nature. Nevertheless, it is probably useful as a basis for interpreting the facts. It allows of both minima and maxima in fluorescence-temperature curves. Examples of the former are not known; they would be expected only at low temperatures.



Anthracene vapour at about 300° has a fluorescence efficiency near unity (Bowen, *Trans. Faraday Soc.*, 1954, 50, 97), and the problem arises of the nature of the degradation process in solution. The work of Porter and Windsor (*Discuss. Faraday Soc.*, 1954, 17, 187) makes it clear that a large part, if not all, of such degradation proceeds *via* the triplet level. The electron spin reversal associated with a singlet-triplet change is most likely to be caused by an element of A^-S^+ structure in the interaction of the excited state with the solvent. The nature of such interactions has been explained by Mulliken (*J. Amer. Chem. Soc.*, 1952, 74, 811). It is difficult to avoid this conclusion even for saturated paraffinic solvents. Those solvents which show reverse temperature coefficients of quenching of anthracene fluorescence are all of a Lewis-base nature. This, together with the well-known strong quenching of the fluorescence by aniline, indicates that in such solvents interactions with excited anthracene molecules are strong and that energy degradation is facilitated.