64. *Solvent Quenching of Fluorescence.*

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Measurements have been made of the effect of temperature on the quantum yield of fluorescence in several solvents, over ranges of about 100°, of anthracene and its 1-chloro-, 1 : 5-dichloro-, 2-methyl, 9-phenyl and 9-cyano-derivatives. Factors affecting the reliability of such measurements are discussed. The results indicate that at higher temperatures the fall-off of fluorescence tends towards dependence only on the anthracene molecule, but that at low temperatures specific solvent influences may predominate.

Earlier work on the apparent quantum yield of fluorescence of solutions of anthracene has shown both positive and negative variations with temperature, which have been interpreted as temperature-dependent solute–solvent interactions.[1] Further examination has brought out the difficulties of obtaining true quantum yields, and requires a reconsideration of the earlier numerical results. In the measurement of fluorescence a beam of light has to be passed into the solution and a part of the fluorescence emission collected. Work involving change of temperature introduces problems of changes of band shapes and of extinction coefficients, changes of concentration due to thermal expansion, changes in the spatial distribution of the emission depending on refractive index, effective removal of dissolved oxygen, stirring, and temperature measurement, and avoidance of deposition of dew on the walls or turbidity in the solutions. For the solutions studied an average value of the change of fluorescence yield for 10° is about 3%; thermal expansion alters the concentration by about 1·2% in this interval, and the refractive index correction is about 1%. The use of rectangular cells with arrangements for the direct measurement of light absorption might appear to be the best way of securing a precisely known amount of excitation. Not only does this lead to great difficulties in the design of apparatus but it would not give accurate results for the very dilute solutions which are desirable to avoid concentration quenching. The existence of the latter effect at once rules out any method making use of total light absorption unless ultraviolet light of wavelength near 2500 Å were used, and this would limit the range of solvents as well as need silica apparatus. For this work, therefore, the concentration of solute was chosen to give "maximum measurable fluorescence" as viewed at 90° to the exciting light beam. At very low concentrations the fluorescence intensity is low because of feeble light absorption; at high concentrations the fluorescence retreats to the front wall and cannot be "seen" by the detector. For monochromatic exciting light there is one concentration giving a maximum collectable fluorescence where the measured intensity is insensitive to concentration variations. It is also insensitive to changes of extinction coefficient, and by working at the concentration appropriate to each solvent the relative comparisons of fluorescence should be obtainable, after a refractive index correction. The allowance to be made for variations of the latter have recently been considered in connection with light-scattering apparatus,[2] and mathematical analysis shows that measured intensities from both rectangular and cylindrical cells should be corrected by a factor close to the square of the refractive index. This not only affects the relation of measurements in different solvents among themselves, but requires a correction due to change of refractive index with temperature. Data on such changes are few and mostly confined to the range just above ordinary temperature. An average value from the literature seems to be somewhat more than a $\frac{1}{3}$% decrease of refractive index for a 10° rise of temperature; we have therefore, assuming the square relationship, corrected the measured results by a factor of 1% increase or decrease for a decrease or increase of 10° from the ordinary temperature (17°). Though this correction is imperfect it cannot greatly change the overall picture of our results.

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[1] Bowen and Cook, *J.*, 1953, 3059; Bowen and West, *J.*, 1955, 4394.

[2] Hermans and Levinson, *J. Opt. Soc. Amer.*, 1951, **41**, 460.

The concentrations used were about 10^{-4}M, where concentration quenching is small or negligible. The possibility of error due to changes in the loss of measurable fluorescence because of reabsorption within the solution (over-lap effect) was explored by making measurements in chosen examples with and without a filter cutting off the shorter-wavelength end of the fluorescence band. No significant differences from this cause were found. Absolute fluorescence yields were obtained from the relative measurements by taking the yield for dilute solutions in benzene[3] as 0·26. Because of the differences of fluorescence-band positions of the different solutions and the non-uniform spectral sensitivity of the photo-multiplier response the absolute values are much less accurate than the relative ones, but the error from neglect of this factor in the blue region is probably less than 10%.

EXPERIMENTAL

The solutions were contained in a small clear Dewar vessel, illuminated on one side by a narrow beam of mercury-lamp light filtered through a Chance OX 1 glass filter, transmitting the group of mercury lines near 3660 Å. The fluorescence, defined by a narrow aperture, was measured by a photo-multiplier in a direction at right angles. A fraction of the exciting beam was diverted by an inclined glass plate to a second photo-multiplier to monitor the light. The multiplier outputs were connected across two equal high resistances with centre-point joined to earth; the two anodes were connected to a sensitive galvanometer which was initially brought to zero by adjustable diaphragms in the light paths. Changes in fluorescence due to temperature were then measured by deflections of the galvanometer from zero. This simple arrangement is strictly balanced for light fluctuations only at the zero, but affords a very delicate way of determining small differences of the fluorescence intensity. The solutions were de-oxygenated by a stream of nitrogen through a fine capillary tube; this, together with movements of the heating or cooling device, served to keep the liquid stirred. Temperature was determined by a copper–constantan thermocouple. Cooling was effected by a dipping copper rod with the upper end fixed into a vessel into which liquid oxygen could be sprayed. To prevent deposition of ice on cooling, the liquids were carefully dried. Heating was effected by a small immersed coil of copper tubing through which steam or hot water could be sent. Particular care was taken to minimise error caused by movement of the reaction vessel, photo-multiplier fatigue, fluctuations in the light intensity and in the high-tension supply to the photo-multipliers, residual fluorescence of the solvent, and evaporation of solution by the deoxygenation process.

RESULTS

9-Cyanoanthracene gave nearly constant fluorescence yields equal to unity between −70° and 20° in hexane and between −30° and 90° in kerosene.

9-Phenylanthracene in hexane between −70° and 10° gave yields F changing from 0·71 to 0·38, closely represented by the equation, $1/F - 1 = 34{\cdot}5 \exp(-1800/\boldsymbol{R}T)$. This is in accordance with a mechanism of a temperature-independent fluorescence emission in competition with a deactivation process of activation energy 1800 cal./mole.

1-Chloro- and 1 : 5-dichloro-anthracene gave yields for paraffin solvents representable by the equations, $1/F - 11 = 76{\cdot}5 \exp(-1620/\boldsymbol{R}T)$ (1-chloro), and $1/F - 14{\cdot}5 = 286 \exp(-2400/\boldsymbol{R}T)$ (dichloro). These results indicate that in addition to a temperature-sensitive deactivation process there is also a temperature-independent one which is doubtless to be associated with the facilitation of singlet–triplet transition by the chlorine atoms.

Table 1 gives the yields for 2-methylanthracene in paraffin solvents. The first series of figures for each solvent gives the intensity ratios directly related to a benzene solution, the second gives the ratios corrected for the difference of refractive index at room temperature between the solvent and benzene, and the third gives them corrected by 1% per 10° to allow for temperature change of refractive index. It will be noted that apparent maxima in the first series are largely flattened out after correction, and it seems that the yields for 2-methylanthracene do not tend to unity at very low temperature but level to a constant value.

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[3] Melhuish, *New Zealand J. Sci. Technol.*, 1955, **37**, *B*, 142.

Table 2 gives results arranged similarly for anthracene dissolved in ester solvents. Here again maxima in the apparent results become limiting values after correction.

Measurements were also made of anthracene dissolved in a series of alcohol and paraffin solvents, the former showing a levelling off of yields at low temperatures, as for the ester solvents. Particularly for the paraffins, however, both the detailed shapes of the fluorescence–temperature curves and the relative intensities between different solvents showed unexpected peculiarities; for instance, in *iso*pentane the yields were markedly lower and appeared to have a different temperature-variation from those in hexane. These effects are believed to be due to the lack of perfect monochromatism of the mercury lines near 3660 Å used for excitation.

TABLE 1. *Yields (F) for 2-methylanthracene.*

Solvent	−90°	−70°	−50°	−30°	−10°	+10°	+30°	+50°	+70°	+90°
Light petroleum ...	0·375	0·397	0·406	0·398	0·38	0·361				
	0·316	0·335	0·342	0·336	0·320	0·305				
	0·348	0·362	0·363	0·349	0·327	0·305				
n-Hexane			0·348	0·359	0·362	0·349				
			0·298	0·307	0·31	0·299				
			0·316	0·32	0·316	0·299				
Kerosene				0·268	0·280	0·288	0·290	0·285	0·278	0·271
				0·239	0·250	0·257	0·259	0·255	0·248	0·242
				0·249	0·255	0·257	0·254	0·250	0·244	0·238

TABLE 2. *Yields (F) for anthracene.*

Solvent	−70°	−50°	−30°	−10°	+10°	+30°	+50°
Methyl acetate	0·321	0·327	0·328	0·322	0·314		
	0·270	0·275	0·276	0·271	0·264		
	0·292	0·292	0·287	0·276	0·265		
Ethyl acetate	0·336	0·347	0·346	0·337	0·325		
	0·286	0·296	0·295	0·287	0·277		
	0·310	0·314	0·307	0·293	0·277		
n-Butyl acetate		0·296	0·303	0·303	0·296		
		0·259	0·265	0·265	0·259		
		0·275	0·275	0·271	0·260		
n-Pentyl acetate		0·266	0·274	0·275	0·270	0·261	
		0·235	0·242	0·242	0·238	0·230	
		0·249	0·250	0·247	0·238	0·226	
Ethyl formate	0·318	0·324	0·324	0·319	0·310		
	0·267	0·272	0·273	0·268	0·261		
	0·289	0·289	0·284	0·273	0·261		
Ethyl butyrate	0·261	0·267	0·269	0·263	0·255	0·247	0·241
	0·228	0·233	0·235	0·230	0·223	0·216	0·211
	0·246	0·247	0·245	0·234	·223	0·212	0·203

The mercury group contains several atomic lines, and on Fig. 1 two of the stronger ones, at 3650 and 3663 Å, are shown by black vertical lines representing their approximate intensity ratio. Curves A and B are portions of the absorption spectrum of anthracene in ethyl alcohol and *iso*pentane solution respectively. For the latter there is a large difference in light absorption for the two lines, and this introduces an error in measurement when the method of " maximum measurable fluorescence " is employed, since different solutions are not absorbing identical amounts of light at their optimum concentrations. Only a rough allowance for this error can be made, but Fig. 2 gives the curves obtained from the results with some attempt at correction. The heavy line is that of the equation $1/F - 1 = 8{\cdot}35 \exp(-750/\boldsymbol{R}T)$. The paraffin solvents fit this curve within the experimental inaccuracy, and the alcohol solvents fit at the higher temperatures. The over-all picture of the results, which are necessarily fragmentary because of the volatility, solidification, etc., of the solvents, is that all the curves appear to run together at higher temperatures and there have a common temperature-dependent deactivation process of about 750 cal./mole. At low temperatures a different form of deactivation is evident, dependent on solvent interactions and increasing in magnitude through the alcohols to the esters and to toluene. This process seems to be almost temperature-independent; the negative slopes for some of the solvents are less than the experimental uncertainty. A scheme of the following type would interpret the results :

$$\begin{array}{rll} \mathrm{A} + h\nu \longrightarrow \mathrm{A}^* & & \\ \mathrm{A}^* + \mathrm{S} \rightleftharpoons \mathrm{A}^*\mathrm{S} & & \text{Eqm. const. } Ke^{Q/RT} \\ \mathrm{A}^* \text{ or } \mathrm{A}^*\mathrm{S} \longrightarrow \mathrm{A} + h\nu' & & k_f \\ \mathrm{A}^* \longrightarrow \mathrm{A} & & k_f k_a e^{-E/RT} \\ \mathrm{A}^*\mathrm{S} \longrightarrow \mathrm{A} + \mathrm{S} & & k_f k_b \end{array}$$

Then $1/F - 1 = k_a \exp(-E/RT)$ at high temperatures and k_b at low temperatures.

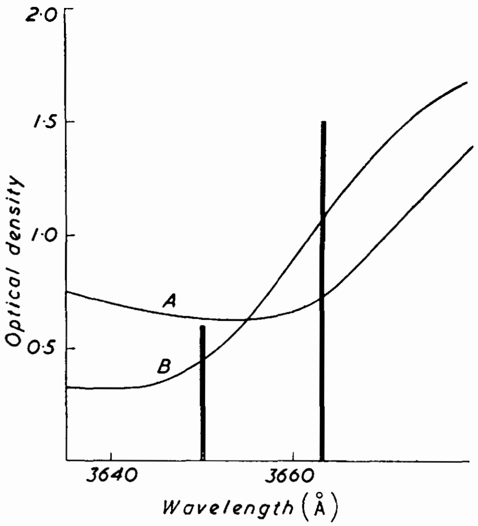

FIG. 1. *Absorption spectrum of anthracene in (A) ethyl alcohol, (B) isopentane near* 3660 Å.

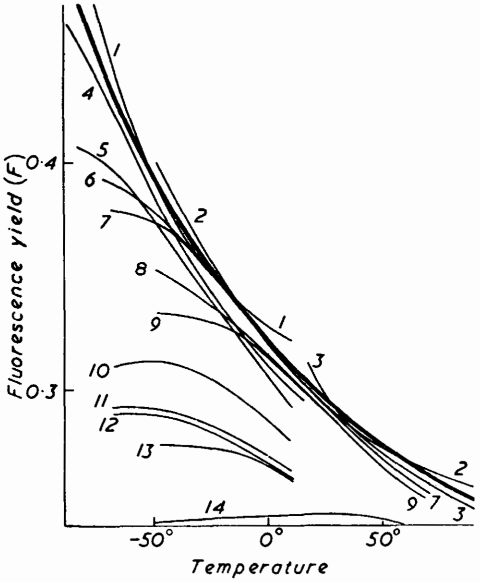

FIG. 2. *Temperature variation of the fluorescence yield of anthracene in several solvents.*

1, *n*-Hexane
2, Kerosene
3, Heavy paraffin
4, Methyl alcohol
5, Ethyl alcohol
6, *n*-Propyl alcohol
7, *n*-Butyl alcohol
8, *n*-Pentyl alcohol
9, *n*-Hexyl alcohol
10, Ethyl acetate
11, Methyl acetate
12, Ethyl formate
13, Butyl acetate
14, Toluene

The low-temperature deactivation process may be associated with π-electron interactions between solute and solvent, so that the intermolecular effect resembles the intramolecular action of a substituted halogen atom in anthracene. On the other hand the high-temperature process seems to be determined by the properties of the anthracene molecule itself. The values of the activation energies E found in this work are significantly near the range of vibrational frequencies of conjugated ring molecules. By analogy with the naphthalene molecule,[4] anthracene would be expected to have low vibrational frequencies of the ring-wagging and out-of-plane type in the range 500—800 cal./mole, as well as bending and distortion types of up to 5000 cal./mole. The " solvated " molecule appears to be restricted in some of these types of vibration, but in the " free " molecule in solution the temperature-activation of certain vibrational modes facilitates the singlet-triplet transition of the excited molecule with corresponding fluorescence quenching.

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[4] Lippincott and O'Reilly, *J. Chem. Phys.*, 1955, **23**, 238.