608. *Temperature Coefficients of Fluorescence.*

By E. J. Bowen and R. J. Cook.

Measurements have been made of the changes of fluorescence intensity with temperature of a series of substituted anthracenes in four organic solvents. The temperature coefficients are in some instances positive and in others negative, and the effects are explained on the basis of intermolecular attractions between solvent molecules and the electronically excited solute molecules.

The fluorescence intensities of six anthracene derivatives, prepared by synthesis and purified by chromatography, have been measured in dilute solution in four organic solvents at temperatures between 15° and 60°. The liquids were contained in a water-jacketed tube for temperature control and illuminated by a narrow beam of 3650 Å radiation. The fluorescence was measured at right angles to the exciting beam by a balanced photomultiplier device as described by Bowen and Metcalf (*Proc. Roy. Soc.*, 1951, *A*, **206**, 437). The concentration of the solute was about 10^{-4}M and fixed at the point where the measurable fluorescence was a maximum owing to the balance between the geometry of the apparatus and the fraction of light absorbed (Bowen and Coates, *J.*, 1947, 105).

The solutions were deoxygenated by passage of a fine stream of coal gas purified by charcoal and silica gel, and the small amount of residual oxygen quenching allowed for from a knowledge of the oxygen content of the gas (0·7% by vol.) and the effect of dissolved air on the fluorescence. The solvents used were "AnalaR" benzene and acetone, B.P. chloroform, and aromatic-free kerosene purified by treatment with fuming sulphuric acid and passage through a column of activated alumina. Within the limits of error fluorescence was found to change linearly with temperature over the small range investigated. The measured intensities were converted into absolute fluorescence efficiencies by comparison with the value 0·24 for anthracene in benzene (Bowen and Williams, *Trans. Faraday Soc.*, 1939, **35**, 765), since all the solutions absorbed the same fraction of the incident light and the wave-length variation of the photomultiplier sensitivity was negligible. The results are given in Table 1.

Table 1. *Fluorescence efficiencies* F *of very dilute solutions of anthracenes, where* F_0 = *efficiency at* 0° and $F = F_0(1 - 10^{-4}\alpha t)$ *up to* t = 60°.

Anthracene		Kerosene	$CHCl_3$	C_6H_6	$COMe_2$	Anthracene		Kerosene	$CHCl_3$	C_6H_6	$COMe_2$
Unsubst.	F_0	0·267	0·090	0·234	0·263	1-Cl	F_0	0·081	0·048	0·079	0·094
	α	6·9	−3·9	−3·1	2·45		α	2·18	−0·82	−0·44	1·67
9-Ph	F_0	0·687	0·458	0·773	0·649	1 : 5-Cl_2	F_0	0·064	0·041	0·073	0·075
	α	34·9	23·6	29·4	19·3		α	1·76	0·29	1·31	1·91
9 : 10-Ph_2	F_0	0·758	0·65	0·80	0·776	9 : 10-Cl_2	F_0	0·746	0·590	0·815	0·741
	α	7·34	0	0	−9·55		α	58	36	46	56

The following facts are apparent. All the efficiencies fall with rising temperature for the substances in kerosene solutions, and fall more steeply than in the other solvents.

Not only are the temperature variations less in benzene, chloroform, and acetone, but in the first two solvents the solutes anthracene and 1-chloroanthracene show an inverse temperature effect, and 9 : 10-diphenylanthracene does so in the last.

In mixed kerosene–bromobenzene solutions of anthracenes the fluorescence is partly quenched by the bromobenzene and the temperature variations sometimes change sign, as shown in Table 2.

TABLE 2. *Fluorescence efficiencies* F *of very dilute solutions of anthracenes in kerosene containing* B *vol.* % *of bromobenzene, where* F_0 = *efficiency at* 0° *and* $F = F_0(1 - 10^{-4}\alpha t)$ *up to* t = 60°.

		B, %						B, %			
Anthracene		0	10	20	40	Anthracene		0	10	20	40
Unsubst.*	F_0	0·267	0·092	0·054	0·028	1-Cl	F_0	0·081	0·040	0·039	0·026
	α	6·9	0	−0·71	−0·89		α	2·18	0·56	0	−0·51
9-Ph	F_0	0·687	0·496	0·435	0·394	1 : 5-Cl_2	F_0	0·064	0·049	0·038	0·028
	α	34·9	31·3	29·8	29·3		α	1·76	0·84	0·20	−0·16
9 : 10-Ph_2	F_0	0·758	0·676	0·641	0·579	9 : 10-Cl_2	F_0	0·746	0·745	0·749	0·746
	α	7·34	7·78	9·78	9·34		α	58	55	54	52

* For $B = 3\%$, $F_0 = 0{\cdot}165$ and $\alpha = 2$.

Increase of fluorescence intensity with increase of temperature, sometimes referred to as a negative temperature coefficient of quenching, has been explained in terms of molecular interactions of molecules in the ground state (Bowen and Coates, *J.*, 1947, 105). Though this undoubtedly occurs in some systems, in these instances interaction between excited solute and normal solvent molecules seems more likely.

FIG. 1.

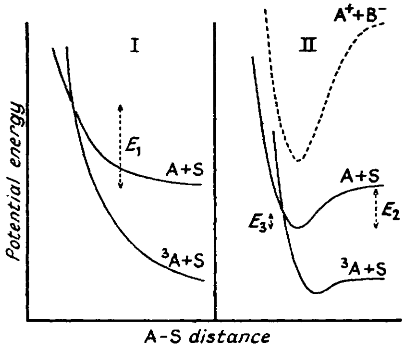

FIG. 2.

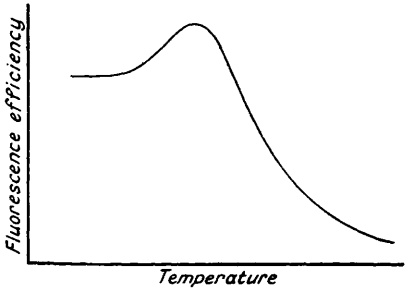

Fig. 1, I, shows repulsional interaction curves between solvent molecules S and fluorescent solute molecules A, the curve for the excited molecule A * crossing one for a lower state, probably the triplet level ^3A, in which energy available for fluorescence is degraded. Quenching then depends on the molecules A* + S having sufficient energy E_1 to rise to the crossing point, and on the efficiency of change over to the other curve at that point.

According to a recent theory by Mulliken (*J. Amer. Chem. Soc.*, 1952, **74**, 811), the proximity of an $A^{+}B^{-}$ interaction curve, as shown broken in Fig. 1, II, causes the A,S interaction curves to develop minima corresponding to the ionic attraction. We may then write the following scheme :

	Rate constant
1. $A + h\nu \longrightarrow A^*$	1
2. $A^* \longrightarrow A + h\nu'$	k_f
3. $A^* + S \longrightarrow {}^3A + S$	$k_d e^{-E_1/RT}$
4. $A^* + S \longrightarrow AS^*$	k_1
5. $AS^* \longrightarrow A^* + S$	$k_2 e^{-E_2/RT}$
6. $AS^* \longrightarrow {}^3A + S$	$k_3 e^{-E_3/RT}$

whence, if F = fluorescence efficiency,

$$1/F = 1 + k_d/k_f e^{-E_1/RT} + k_1 k_3/k_f(k_2 e^{(E_3 - E_2)/RT} + k_3)$$

This presupposes that A* is quenched in two different ways, by reaction (3) of unoriented molecules, and by reaction (6) of an oriented molecular complex. The kinetic treatment of such a scheme is hampered by lack of knowledge of collision processes in liquids. It is sometimes assumed that collisional rates between solute and solvent molecules decrease with rising temperature in a manner proportional to the viscosity (Moelwyn-Hughes, " Kinetics of Reactions in Solution," Clarendon Press, 1933, p. 20); on the other hand encounter rates are inversely proportional to the viscosity divided by the absolute temperature (Umberger and LaMer, *J. Amer. Chem. Soc.*, 1945, **67**, 1099). If reactions (3)—(6) depended directly on the viscosity, their rate constants would include a temperature dependence of $e^{E/RT}$, where $E = 3{\cdot}3$ kcal. for kerosene as an example. That this is unlikely is shown by several considerations. Inverse temperature coefficients of quenching might then be found in solvents of high viscosity change, instead of being associated with solvents of molecular complexing type. It is also relevant that anthracene has practically the same fluorescence efficiency and temperature coefficient of fluorescence in saturated aliphatic paraffin solutions of viscosities varying by a 300 : 1 ratio and of viscosity temperature coefficients varying by a factor of 14 (Metcalf, D.Phil.Thesis, Oxford, 1950). We shall therefore assume for simplicity that the frequency factors of all the reactions are independent of temperature, and that the exponential factors relate to energies of the potential-energy diagram. The scheme then gives an F–T curve of the shape shown in Fig. 2 (assuming $E_2 > E_3$).

Experimental data for a single solution covering all the features of such a predicted curve have not yet been obtained, because of the practical difficulties of measurement over a very wide temperature range. The results of Tables 1 and 2, however, may well represent small segments of curves of Fig. 2 type, including the modification without a maximum where $E_2 < E_3$. Further progress in this field needs a better understanding of kinetic interactions of solute and solvent molecules, as well as more extended measurements on suitably chosen systems.

PHYSICAL CHEMISTRY LABORATORY, UNIVERSITY OF OXFORD. [*Received, May 8th*, 1953.]