644. *The Effect of Viscosity on the Fluorescence Yield of Solutions.*

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The fluorescence yields of several solutes in ethylene glycol, water–glycerol and water–sucrose solutions have been measured, and found to increase with increasing viscosity of the liquid. The effect, however, is very dependent both on the solute and on the nature of the solvent.

IT has been found recently that the quantum yields of fluorescence of dilute solutions are raised if the viscosity of the solvent is increased.[1,2] This effect is to be distinguished from the influence of high viscosity in diminishing collisions in a solution between fluorescent molecules and active quenching agents, such as unexcited molecules or dissolved oxygen.[3] The functional relation between yield F and solvent (macro) viscosity η is still imperfectly known. For diphenylmethane dyes in aqueous glycerol–dextrose solutions the process of electronic energy degradation is proportional to $1/\eta$ while for *meso*-substituted anthracene derivatives in paraffins it is proportional to $1/\eta^{0.25}$. Expressing it empirically as $1/\eta^n$ we have $F = \eta^n/(\eta^n + \text{constant})$. A number of other fluorescent solutes in water–glycerol or –sucrose solutions and in ethylene glycol have been examined for viscosity effects.

The concentrations (about 10^{-4}M) of fluorescent solute were adjusted to give equal values (0·1) of the product of extinction coefficient and concentration for the exciting light of wavelength 3660 Å, so that each solution absorbed the same (small) fraction of the incident light beam. Fluorescence emerging at 90° to the exciting beam from a small rectangular cell of the solution was collected by the slit of a constant-deviation spectrometer, fitted with a photomultiplier, so that the fluorescence spectrum could be obtained. By calibration, a lamp of known colour temperature being used, the spectra were plotted as wave-number against relative numbers of quanta emitted per equal interval of wave-number, so that areas were true measures of relative fluorescence yield. Corrections for refractive-index differences were made[4] by multiplying by (refractive index).^{2}

Errors due to re-absorption of fluorescence were insignificant at the concentrations used. Absolute yields were obtained by comparison with a solution of sodium 4-aminonaphthalene-1-sulphonate in 97% glycerol, for which F is close to unity. The above

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[1] Oster and Nishijima, *J. Amer. Chem. Soc.*, 1956, **78**, 1581.
[2] Bowen and Sahu, *J. Phys. Chem.*, 1959, **63**, 4.
[3] "Fluoreszenz Organischer Verbindungen," Fōrster, Göttingen, 1951, p. 192.
[4] Hermans and Levinson, *Amer. J. Opt. Soc.*, 1951, **41**, 460.

empirical law was found to hold approximately for viscosities that are not too high; at very high viscosities polarization due to non-rotation of the excited molecules reduces the intensity observable at 90° to the incident light beam. Table 1 gives values for F and n.

TABLE 1. *Sodium salts in water–glycerol* (*G*) *and water–sucrose* (*S*) *solutions.*

	F (water)	n (G)	n (S)
4-Aminonaphthalene-1-sulphonate	0·71	0·95	0·11
5-Aminonaphthalene-1-sulphonate	0·11	0·24	
8-Aminonaphthalene-2-sulphonate	0·27	0·16	
8-Aminonaphthalene-1-sulphonate	0·03	0·24	
2-Aminonaphthalene-1-sulphonate	0·10	0·21	
5-Aminonaphthalene-2-sulphonate	0·56	0·17	
7-Aminonaphthalene-1,3-disulphonate	0·73	0·15	
5-Dimethylaminonaphthalene-1-sulphonate	0·38	0·41	0·18
8-Dimethylaminonaphthalene-2-sulphonate	0·22	0·53	
Anthracene-2,6-disulphonate	0·51	0·13	
Anthracene-2,7-disulphonate	0·20	0·07	

From these results it appears that the viscosity dependence, as measured by the n value, varies greatly for different solutes, in a way unrelated to the magnitude of F, and that it also varies with solvent. To examine the latter point, measurements were made of fluorescence yields in four solvents of equal viscosity (20 cp. at 20°), ethylene glycol, glycerol–water (70·2% of the former by weight), a sucrose–water solution (52·4% of the former by weight), and a solution of the cellulosic polymer " Cellofas B " in water. Table 2 gives the results.

TABLE 2. *Values of F for solutions of viscosity* 20 *cp. at* 20°.

Solute	Ethylene glycol	Glycerol–water	Sucrose–water	Cellofas B–water	(Water (viscosity = 1 cp)
Sodium 4-aminonaphthalene-1-sulphonate	0·98	0·94	0·79	0·71	0·71
Sodium 5-aminonaphthalene-1-sulphonate	0·51	0·24	0·15	0·11	0·11
Sodium 5-dimethylaminonaphthalene-1-sulphonate	0·70	0·63	0·51	0·38	0·38
2-1′-Naphthyl-5-phenyloxazole	0·78	0·55	0·19	insol.	insol.

For each solute, the first three columns are not equal, although the solvents had equal macro-viscosities. There is a steady fall in F values across the Table. The results can be interpreted on the following lines. The four solvents from left to right have increasing differences between their macro- and micro-viscosities due to increasing " structural " effects. A " Cellofas B " solution is an extreme example; it contains relatively large aqueous regions of low viscosity associated with polymer chains which enhance the macro-viscosity, while ethylene glycol is more homogeneous on a molecular scale. For a non-radiational change-over of an excited molecule to the triplet or ground level, some particular configuration must be achieved, and one part of the molecule may then be regarded as undergoing a diffusion process with respect to another. In a medium of nonhomogeneous micro-viscosity, these movements may be free to occur in the regions of lower viscosity, and the apparent dependence of deactivation on a power less than unity of the reciprocal macro-viscosity may be an empirical expression of this. It is noteworthy that in some instances the value of n approaches unity (Table 1 and ref. 1), indicating that the effect is fundamentally of diffusional character. The variation of n with solute in any one solvent, however, cannot yet be related intelligibly to differences in molecular structure.

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