

Effect of solvent on polarization of fluorescence of acriflavine.

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(Received 15 January 1976)

The polarization of fluorescence of molecules in solution has been reported to depend upon various factors viz viscosity of the solvent (Perrin 1926), migration of the excited state from the originally excited molecule to a neighbouring molecule (Weber 1953, 1960), shape and size of the fluorescent molecule (Rath & moment/Machwe 1967), temperature etc. The present report deals with the effect of dipole dielectric constant of the solvent as an extrinsic cause of depolarization. The polarization of acriflavine in different solvents (concentration $\sim 10^{-5}$ g/lw) has been measured at room temperature ($\sim 20^\circ\text{C}$) with an Aminco Bowman Spectro photo fluorometer. The effect of scattered light and back ground for each solvent was checked by using pure solvent in the cell and setting the excitation and emission monochromators at values used in polarization measurements. The contribution of this effect to the intensity of fluorescence was found to be less than 0.5%. The results obtained for polarization along with the peak excitation and emission wavelengths and the relative intensity of fluorescence are given in the table below. The dipole moment, dielectric constant and viscosity for the solvent are also included in table 1.

Table 1

Sr No.	Solvent	Dipole moment	Dielectric constant	Viscosity (η)	λ_{ex} (nm)	λ_{em} (nm)	Intensity	P%
1.	Water	2-3	80	1.002	454	500	43	2.0
2.	Formamide	3.25	109	3.307	464	498	63	4.5
3.	Acetone	2.88	20.2	0.316	462	490	75	1.7
4.	Pyridin	2.30	12.5	0.974	464	500	54	2.3
5.	n-Butanol	1.67	17.1	2.900	464	490	87	4.8
6.	Ethanol	1.70	24.3	1.197	464	490	99	4.8
7.	Chloroform	1.10	5.0	0.569	460	506	22	3.0
8.	Methanol	1.65	32.0	0.594	464	490	81	2.2

From table 1 it is seen that the observed variation in polarization can not be accounted for as viscosity effect alone because in this case a plot between $1/P$ and $1/\eta$ (Perrin-1926) will not be linear. Also as the concentration is low, the electromagnetic coupling of neighbouring molecules and its effect on decrease in polarization due to energy migration is small. It is therefore likely that the observed polarization variation is due to dipole moment/dielectric constant of the solvent. The observed variation in polarization in the solvents listed in the table show that the percentage polarization is lower in a solvent

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of higher dipole moment/dielectric constant. Though the solvents chosen have low viscosity, even then some change in percentage polarization may be there due to change of viscosity. However, a comparison between the values of P for solvents of nearly the same viscosity clearly establish the effect of dipole moment/dielectric constant. In the case of chloroform and methanol where the viscosities are of nearly the same order, the percentage polarization in chloroform (lower dipole moment) is higher than in methanol (higher dipole moment). Comparing the relative intensities of polarized fluorescence, the intensity in chloroform is lower than that in methanol, which indicates the presence of non-radiative transfer of energy. In the absence of non-radiative energy transfer the observed polarization would have been much higher, and this can be accounted for only on the basis of the effect of dipole moment/dielectric constant. Similarly, in the case of ethanol and water, the viscosities are again of nearly the same order but the percentage polarization in ethanol is higher than in water. In other cases also like *n*-butanol and formamide, acetone and pyridine, pyridine and water, the observed variation in percentage polarization can be accounted for as due to the dipole moment/dielectric constant. The effect can be explained as follows:

During the short interval of time in which the absorption of excitation energy takes place, the dipole moment of the solute molecule remains unchanged. But just before a radiative transition takes place, the solute molecule gets itself re-oriented in the surrounding solvent medium due to dipole-dipole interaction to get a new equilibrium position. Thus resulting in fluorescence depolarization. The Brownian rotation tends to destroy this equilibrium orientation and causes further depolarization. If the dipole moment of the solute molecule in the excited state is different from that in the ground state, the orientation of the molecule in the equilibrium excited state will be different from the Frank-Condon excited state. Therefore the Brownian rotation will add to the dipole-dipole interaction thereby increasing the depolarization with a consequent decrease in the value of polarization. The dipole-dipole interaction for a given solute depends upon the dipole moment/dielectric constant of the solvent.

The authors are thankful to Prof. L. S. Kotlyari, Deptt. of Physics and Astrophysics, Delhi University, Delhi, for providing the necessary facilities to carry on the experimental work.

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